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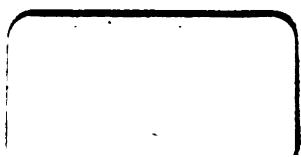
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DEPARTMENT OF COMMERCE

Vol. 11

No. 1

BULLETIN

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

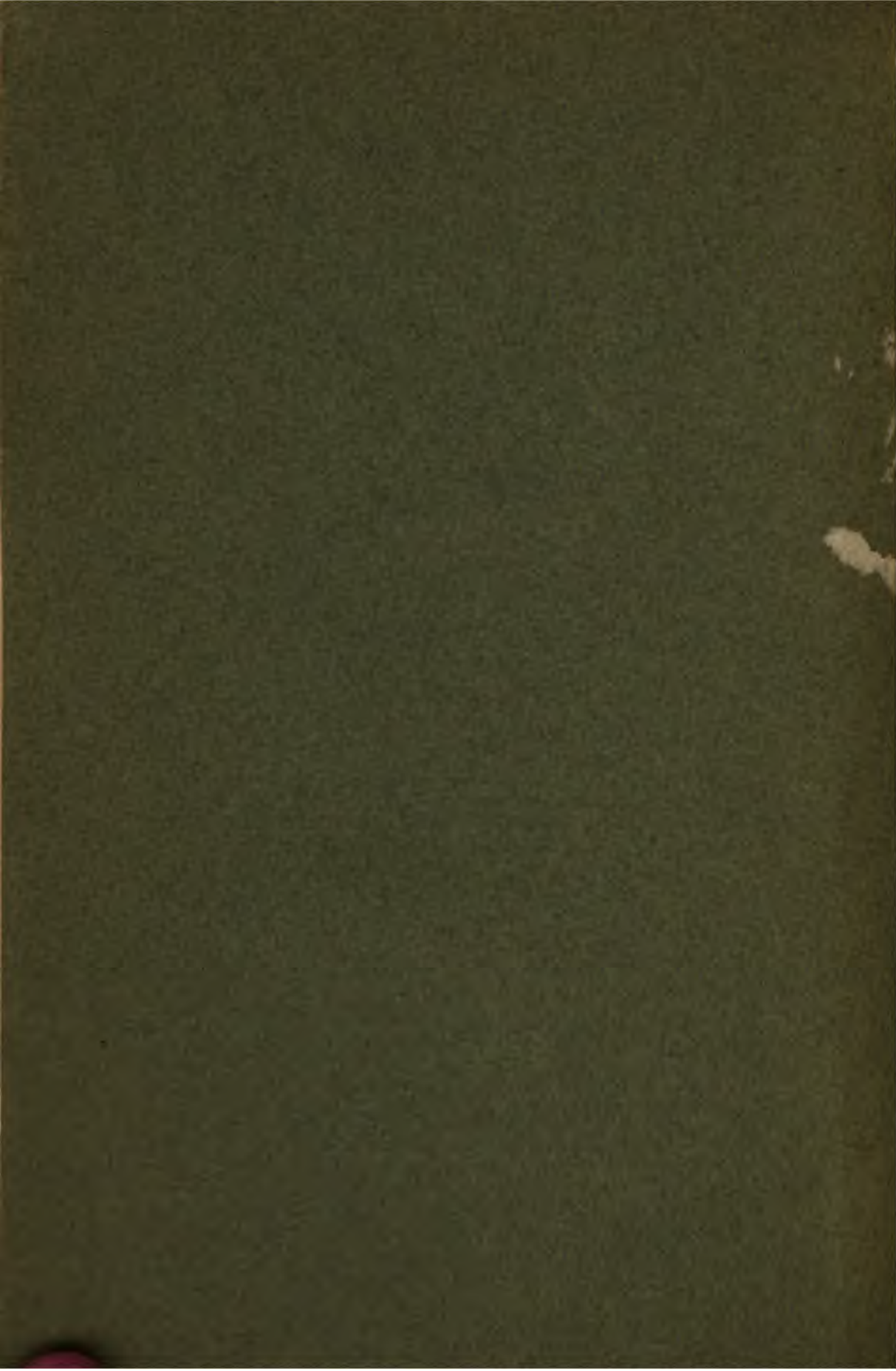
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BULLETIN

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

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1915



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THE TESTING OF POTENTIOMETERS

By Frank Wenner and Ernest Weibel

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I. INTRODUCTION

Potentiometers are being used extensively in electrical measurements in which the precision required is higher than can be obtained by the use of deflection instruments. With a potentiometer and a standard cell, electromotive forces are measured directly. By the use of a standard resistance in connection with the potentiometer and standard cell, measurements may be made from which the current or power may be calculated. If in addition the time is measured we have data from which the energy may be calculated.

In general, potentiometers are constructed very much like other resistance apparatus. They are made up of a number of coils of wire of various resistances connected in various ways. Dial switches, plugs, or sliding contacts are provided to make the necessary changes in the connections to the various coils. The coils are usually made of manganin wire and are adjusted so that the resistances are nearly proportional to the readings of the dials.

In measuring electromotive forces (or potential differences) with a potentiometer, the ratio of the unknown electromotive force to the known electromotive force is determined from the ratio of two resistances, which during the measurement carry a current. (See Fig. 1.) The drop in potential in one resistance, R_s , is made equal to the known electromotive force, S , usually by adjusting the current, I , the equality or balance being indicated by a zero deflection of the galvanometer. This gives

$$S = R_s I$$

The other resistance R_o is adjusted so that its drop of potential balances the unknown electromotive force E . This gives

$$E = R_o I$$

Therefore

$$E = SR_o/R_s \quad (1)$$

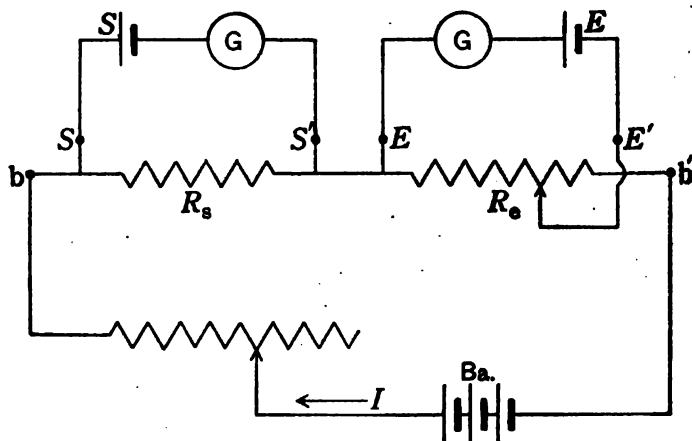


FIG. 1.—Connections for comparing two electromotive forces by potentiometer method

The test therefore consists in making such measurements as are necessary for the determination of the ratio of R_o to R_s for all settings of both R_o and R_s .

When a potentiometer is used in conjunction with a standard resistance and standard cell for determining the current or power, the measurement with the potentiometer is in reality that of a potential difference. The test just referred to is therefore all that is required.

The resistance of the coils is not always accurately adjusted, nor does it remain constant but changes somewhat with time. The greatest change occurs within one year after construction and may amount to as much as several hundredths per cent. Later the changes seldom amount to as much as one hundredth per cent during a year, in well-constructed potentiometers. Therefore potentiometers which are to be used in measurements of high precision¹ should be calibrated occasionally, especially during the first few years. If this is done and the corrections applied, errors on account of lack of adjustment of the coils or on account of changes in their resistance can be eliminated.

A number of potentiometers are tested each year at the Bureau of Standards. These include potentiometers tested for manufacturers, public-service companies, educational institutions, the State governments and various departments of the National Government. Potentiometers of the Feussner² type (see Fig. 2) and Crompton³ (or slide wire) type (see Fig. 5) are the more usual, but occasionally potentiometers of the Raps⁴ type or potentiometers of the split circuit⁵ type, usually designed for use with thermocouples, are tested. The testing of these required a considerable amount of work on account of its having been necessary to make several kinds of measurements on each potentiometer and to use different methods for different types of potentiometers. For this reason the testing of potentiometers has received special consideration.

The purpose of this paper is to bring to the attention of students and users of potentiometers work done at the Bureau of Standards in connection with the testing of such apparatus. To do this we shall (a) discuss the theory of the potentiometer in such a way as to show the corrections which must be applied if results of a high accuracy are to be obtained, (b) describe briefly methods and arrangements used in testing potentiometers, and (c) describe apparatus designed for and used in testing potentiometers.

¹ That is, where the accuracy is 1 in 10 000 or better.

² *Za. f. Instrk.*, 10, p. 113; 1890.

³ *Electrician*, London, 81, p. 32; 1893.

⁴ *Elektrotech. Zs.* 18, p. 215; 1895.

⁵ Dieselhorst: *Za. f. Instrk.*, 26, p. 173-197, 1906; 28, p. 1; 1908.

White: *Phys. Rev.*, 25, p. 334; 1907.

2. THEORY AND CORRECTIONS OF POTENTIOMETERS

Any potentiometer can be considered to be a system or network of conductors having three ⁶ pairs of terminals. The battery or other means of supplying a current, I , to the potentiometer is connected to one pair, the I -terminals; the known or standard electromotive force is connected to the second pair, the S -terminals; and the unknown electromotive force is connected to the third pair, the E -terminals. The current I flowing through the resistance of the potentiometer causes a difference in potential, E , between the E -terminals and, S , between the S -terminals. The ratio of E to I is equal to the resistance R_e and the ratio of S to I is equal to the resistance R_s .

The resistance between the battery terminals, the total resistance of the potentiometer, is designated by the letter T . By manipulation of the various switches, R_e and R_s can be changed but the total resistance T remains approximately constant and would remain constant if the potentiometer were mechanically perfect and correctly adjusted.

In comparing two electromotive forces, one, whose value is usually known and which we shall call S , is connected to the S -terminals and either the resistance R_s or the current I adjusted so that

$$R_s I = S,$$

then the other electromotive force, usually of an unknown value and which we shall call E , is connected to the E -terminals and the resistance R_e adjusted so that

$$R_e I' = E.$$

Therefore

$$E = S R_e I' / R_s I, \quad (2)$$

which differs from the simple case considered above in that the total current through the potentiometer is not necessarily the same when the two balances are made. In order to express the value of E in volts it is therefore necessary to know the value of the ratio $R_e I' / R_s I$ and the value of S in volts.

⁶ For convenience a switch and a fourth pair of terminals are provided for connecting a galvanometer either into one of the leads to the E -terminals or into one of the leads to the S -terminals. In some cases more than one pair of E -terminals are provided and in other cases in effect the E -terminals and S -terminals are identical. (See p. 10.)

The value of S is determined by comparison with the electromotive force of Weston Normal Cells set up according to definite specifications; but as the standard cell constitutes no part of the potentiometer it need not be considered further here. What we shall be concerned with, then, is the determination of the ratio of $R_o I'$ to $R_s I$. A complete calibration consists in the determination of this ratio for all possible values of both R_o and R_s .

In most potentiometers the total resistance is nearly independent of the value of both R_o and R_s , so that if the conditions in the external battery circuit are constant the current will be nearly constant. In any case the ratio I'/I is nearly unity and depends only slightly on the values of R_o and R_s , so we can say

$$I'/I = 1 + h \quad (3)$$

where h is a small correction, which is different for different values of R_o and R_s . Therefore

$$E = SR_o(1 + h)/R_s \quad (4)$$

If the electromotive force of the source supplying the current is constant, we have

$$\frac{I'}{I} = \frac{T_s + R}{T_o + R} \quad (5)$$

or

$$h = \frac{T_s - T_o}{T_o + R} \quad (6)$$

where T_s is the total resistance of the potentiometer at the first balance and T_o is the total resistance of the potentiometer at the second balance and R is the resistance external to the potentiometer.

In many cases, for example potentiometers of the Crompton type, it will be evident from the construction that the total resistance is constant. In other cases, where when a dial switch is changed by one step a resistance is removed from one part of the circuit and another resistance inserted in another part of the circuit for the purpose of keeping the total resistance constant, a few measurements of the total resistance for certain values of R .

and R_s will be required. If these show that h is negligibly small⁷ for all values of both R_o and R_s , the potentiometer is said to be compensated.

In such a case the ratio $R_o I'$ to $R_s I$ is equal to the ratio of R_o to R_s . Compensation, therefore, makes the apparatus much easier to calibrate, as well as much more convenient to use. From this point on, unless the matter is specifically mentioned, we shall assume that the potentiometer under consideration is compensated.

The resistances R_o and R_s are usually varied by the manipulation of three sets of switches, which may be of various forms, including plugs and contacts on a slide wire. These three sets may be called the e -switches, the s -switches, and the f -switches (range or factor switches), and we shall call the reading corresponding to their settings e , s , and f .

The e -switches change the value of R_o over a large range, the s -switches change the value of R_s usually over a small range, and the f -switches change the value of R_o or R_s , or both, by a factor, usually .1 or 10.

If the resistance R_o is independent of the reading s , if the resistance R_s is independent of the reading e , and if a change in the reading f changes the ratio of R_o to R_s corresponding to any reading of e and of s by the same proportional amount as that corresponding to any other reading of e and of s , as is usually the case (even in potentiometers which are not completely compensated), then all possible values of the ratio of R_o to R_s can be determined from a number of measurements equal to the number of possible readings of the e -switches plus the number of possible readings of the s -switches plus the number of possible readings of the f -switches. It will therefore be convenient to introduce into our equation expressing the relation between the unknown and known electromotive force three corrections, one for each of the readings e , s , and f .

The e -switches are regularly so marked that the reading e is approximately proportional to the resistance R_o , so we may write

$$R_o = K(e + a) \quad (7)$$

⁷ In precision measurements, an error, to be negligibly small, must usually be less than 1 in 10 000 and in some cases less than 1 in 100 000.

where K is a constant and a is a small correction depending upon the reading e .

Also the s -switch is so marked that the reading s is approximately proportional to the resistance R_s , so we may write

$$R_s = K's(1 - b) \quad (8)$$

where K' is a constant which may or may not be the same as K and b is a small correction. We therefore have

$$E = \frac{S K}{s K'}(1 + b)(e + a) \quad (9)$$

Here and in the equations which follow we neglect the second and higher powers and products of all small quantities.

Now if we let

$$K/K' = f(1 + d) \quad (10)$$

where f , the reading of the range or factor switches is a simple number, usually an integral power of ten, and d is a correction which is small in potentiometers of good design and construction, we have

$$E = f(1 + b + d)(e + a)S/s \quad (11)$$

In potentiometers having only one range there is no range or factor switch to be read, consequently a value for f must be supplied. This value is always to be taken as the nominal number of volts per unit of the reading e . Thus, for a potentiometer in which the reading e gives the resistance R_s in ohms the value of f to be supplied is the nominal number of volts per ohm. A better arrangement in this case would be to choose the unit of the reading e so as to make f unity, in which case the reading e is in volts.

In some cases it may not be possible to make the reading s equal to the value S of the known electromotive force. It is therefore necessary to introduce a correction c which may be defined by the equation

$$S/s = 1 + c \quad (12)$$

so we have

$$E = f(1 + b + c + d)(e + a) \quad (13)$$

Some potentiometers are not provided with s -switches and the difference between the value of the known (or standard) electromo-

tive force and the standard cell value for which the potentiometer is adjusted may be fairly large. In such cases the correction c is of importance and must regularly be applied. To illustrate the application of the correction c , suppose that the potentiometer has no standard cell dial, but is adjusted for use with a standard cell whose voltage is 1.0185 and we wish to use it with a standard cell whose voltage is 1.0190. This makes

$$S = 1.0190 \text{ volt and } s = 1.0185 \text{ volt}$$

so

$$c = \frac{1.0190 - 1.0185}{1.0185} = +.0005$$

Since the three corrections a , b , and d corresponding to any readings e , s , and f are in effect but a single correction, which, when applied to fe/s gives the ratio of the resistances R_e to R_s , two of these corrections may be chosen more or less arbitrarily, providing a proper value is assigned to the third. In the use of the potentiometer the corrections are more conveniently applied if d is made zero for that reading of f which is most used and if b is made zero for that reading s which is most used. Ordinarily* b is taken as zero for $s = 1.0185$ and in a well-constructed instrument this usually makes b negligibly small for values of s near 1.0185. In this way the entire correction for the readings most used is included in a and is therefore easily applied, since it is added directly to the reading e .

The reading e is that corresponding to the settings of the e -switches (dial switches or dial switch and slide wire). Since each of the e -switches changes R_e by amounts approximately proportional to changes in their readings we can say that

$$e = e_1 + e_2 + e_3 + \text{etc.} \quad (14)$$

where e_1 is the reading of the first switch, i. e., the one which changes R_e in the largest steps, e_2 is the reading of the second switch, i. e., the one which changes R_e in the next largest steps, etc. If the change in resistance R_e corresponding to a change in reading of

* The reason for choosing 1.0185 is that the electromotive force of the Weston Normal Cell at 20°C. is 1.0183 and that of the Weston unsaturated or portable cell is, on the average, about 1.0187 volt.

any one of the switches is independent of the readings of all of the other switches⁹, as it usually is, we can say that

$$a = a_1 + a_2 + a_3 + \text{etc.} \quad (15)$$

where a_1 depends upon the reading e_1 ,

where a_2 depends upon the reading e_2 ,

where a_3 depends upon the reading e_3 , etc.

We may therefore write the complete formula, expressing the value of the unknown electromotive force in terms of the readings of the potentiometer and corrections, as follows:

$$E = f [(e_1 + a_1) + (e_2 + a_2) + (e_3 + a_3) + \text{etc.}] (1 + b + c + d). \quad (16)$$

Here f is the reading of the range switch and d is its correction; e_1 is the reading of the first dial and a_1 is the correction to this reading; e_2 is the reading of the second dial and a_2 is its correction; e_3 is the reading of the third dial and a_3 is its correction, etc.; b is a correction to be applied on account of errors in the adjustment of the resistance R_s ; and c is the amount in proportional parts by which the known electromotive force exceeds the reading s (either the reading of a standard cell dial switch, or the standard electromotive force for which the potentiometer is adjusted).

In the case of potentiometers of the Crompton type the reading e_2 is that corresponding to a setting of the contact on the slide wire. In such instruments usually 100 or 1000 divisions of the slide wire are equivalent to a step of the dial switch. If a reading of 1000 on the slide wire is equivalent to a reading of 0.1 on the dial (as is the case with the Leeds and Northrup potentiometer), we must consider that

$$e = e_1 + .0001e_2. \quad (17)$$

Since a_1 , a_2 , and a_3 , etc., for any particular reading, are in effect a single correction, it is possible to choose all but one arbitrarily if the proper value is given to the one. It has been found convenient to choose a_3 , a_4 , etc., zero for the reading $e = 0$.

In some potentiometers it is necessary to change the f reading after balancing the known electromotive force and before balancing the unknown electromotive force. In this case the second reading

⁹ This is not necessarily the case in potentiometers in which the Kelvin-Varley shunt scheme is used, nor in split circuit potentiometers unless the adjustment is very good.

of f divided by the first reading of f usually gives the value of f to be used.

In general equation (16) applies only in case the potentiometer is compensated, but if the known and unknown electromotive forces can be balanced without changing any of the e , s , or f -switches between balances, or if the balances can be made simultaneously, the corrections just considered are all that are necessary even though the potentiometer is not compensated.

However, as a matter of convenience, it is desirable that potentiometers be compensated so that changes in the settings of the dials do not change the total resistance by an appreciable amount. Should there be a decided lack of compensation, the simultaneous balance of both electromotive forces could be made only by successive approximations since an adjustment of R_s to balance against E would change the current and thus disturb the balance against the known electromotive force and then a change in current to reestablish this balance would disturb the balance against the unknown electromotive force.

In some potentiometers the known and unknown electromotive forces are in effect alternately connected to the same terminals so that the s and e -switches are identical. In this case

$$R_s = K (e_s + a_s) \text{ instead of } K's(1 - b)$$

so that $b = -a_s/e_s$ and formula (13) becomes

$$E = f (1 - a_s/e_s + c + d) (e + a) \quad (18)$$

This formula ¹⁰ applies only if the potentiometer is compensated.

In general then the test of a potentiometer consists in determining the corrections a_1 , a_2 , a_3 , etc., b and d for all possible reading of s , f , e_1 , e_2 , e_3 , etc. In the case of a 5-dial potentiometer (5 e -dial switches each having 10 steps or 11 points) if the s -dial switch has 20 points (19 steps) and if there are two ranges or two readings for f , the total number of corrections is 77. In this case the possible number of settings of the ratio R_s to R_x or readings of the potentiometer is 6 442 040 to each of which the correction to be applied is obtained from the 77 corrections, one for each reading of each of the switches.

¹⁰ If there is no factor switch, or if its reading is the same for both balances, then $f=1$ and $d=0$.

3. METHODS OF TESTING

Since the test of a potentiometer must give the corrections to be applied to the readings to give the values of the electromotive forces measured, a simple and direct method is to use another potentiometer to furnish known electromotive forces. If these are measured by means of the potentiometer to be tested the corrections can be readily calculated. This method requires a potentiometer which has been previously calibrated and requires that two currents (one in each potentiometer) be maintained constant. For these reasons this method has been little used in the Bureau of Standards, though it has the advantage of giving the corrections directly and under operating conditions.

The method commonly used is to measure the relative values of the component resistances of the apparatus and from these to calculate the corrections. For the measurement of the relative values of the resistances a bridge is almost always used. Some of the bridge arrangements which have been used by the authors are described below.

The ratio of the resistances R_s and R_x can be determined either by direct measurement or by calculation from the measurement of the component parts; that is, the individual resistance coils or sections. To measure the resistances R_s and R_x directly requires apparatus whose corrections are known to an accuracy at least as high as that sought in the calibration of the potentiometer. If R_s and R_x are to be calculated from the values of their component resistances, the more important measurements should be comparisons of nearly equal resistances. We are therefore mainly concerned with the small differences between the different steps or coils so in general it is not necessary that we know accurately the corrections to the readings of the apparatus used in making the measurements. Good apparatus for which the corrections were sufficiently well known to permit of measuring R_s and R_x directly has not always been available. In general it has been our aim, therefore, to use such arrangements as will give the corrections to the readings of the potentiometer to an accuracy higher than that to which the corrections for the apparatus used in making the test are known. Some of the arrangements may therefore be suitable for use in

those laboratories in which there is but a small amount of accurately adjusted or calibrated resistance apparatus.

Feussner Type.—The connections of a potentiometer of the Feussner type as improved by Brooks and made by O. Wolff are shown diagrammatically in Fig. 2. The relative values of the 1000 and 100-ohm coils in the first and second decades are measured in a Wheatstone bridge using the substitution method. If 1000 and 100-ohm resistance standards whose corrections are accurately known are available, they should be included in the measurements

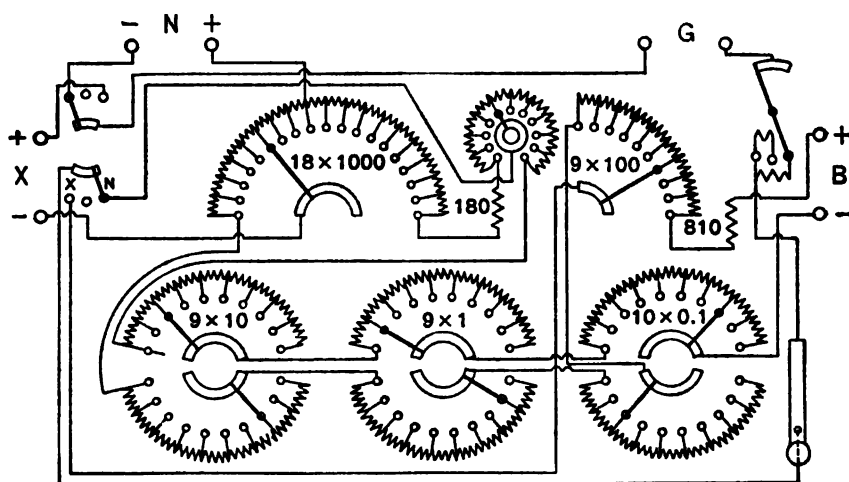


FIG. 2.—Diagram of Wolff potentiometer

of the 1000 and 100-ohm sections of the potentiometer. In this method the coils are connected successively in the same arm of the bridge and the changes in the setting of the bridge necessary to reestablish the balance are noted. The connections to the coils are made through flexible leads attached to the contact blocks by means of screws. If care is taken in making the screw connections the total connection resistance will be sufficiently constant, so that the changes in setting of the bridge will represent differences in the resistances of the coils. Since these differences are small the relative values of the resistances may be determined to a high accuracy with but a limited knowledge concerning the other resistances in the bridge.

In order to get the relative values of all of the coils, $\Sigma 1000$ ohms (i. e., 1000 ohms resistance made up from the 100, 10, 1, and .1-ohm coils) is measured along with the 1000-ohm coils, also $\Sigma 100$ ohms, made up from the 10, 1, and .1-ohm coils, is measured along with the 100-ohm coils. The 10, 1, and .1-ohm coils are measured in a Wheatstone bridge in the ordinary manner; that is, the three decades are connected into a Wheatstone bridge and the total resistance corresponding to the various settings of the dials measured. From the resistance corresponding to the different readings it is necessary to subtract the resistance found with the three dials set at zero. The odd part of the resistance across which the standard cell is balanced is also measured in a Wheatstone bridge in the ordinary manner.

In the 10, 1, and .1-ohm decades, double dials with compensating coils are used to maintain a constant total resistance. In checking the constancy of the total resistance all the coils except those in the three double decades are short circuited and the total resistance corresponding to the various settings of the double dials is then measured in a Wheatstone bridge. It will be noted that in all cases where measurements depend directly upon the accuracy of the bridge the quantity measured is less than 2 per cent of R_0 or less than 2 per cent of R_0 when $e_1 = 5000$ or more.

Besides the resistance in the various decades there may be an appreciable resistance in the connections between them, which would require a correction to be applied when the potentiometer was set to read zero. In this case a_1 for $e_1 = 0$ is the resistance R_0 when e_1, e_2, e_3 , etc., each equals zero. To determine this correction, which usually is small, the potentiometer is connected as it is in use, except that the E -terminals are short-circuited and a switch is included in the connection to the battery. When the e -switches all read zero, on closing the switch to the battery there will be a deflection of the galvanometer depending upon the magnitude of R_0 and the magnitude of the test current. The resistance R_0 is then obtained by comparing this deflection with the change in the deflection produced by changing the setting by a small amount (say one step on the lowest dial). Since the connections between the various decades include several switches, the

constancy of this correction is a measure of the reliability of the dial switches.

A modification of the Carey-Foster method has also been used in measuring the 1000 and 100-ohm coils. With the connections as shown in Fig. 3*a* and with the galvanometer connected to g_1 , a balance is made by changing either of the nearly equal ratio arms A or B . Then with the standard S and the link L interchanged and the galvanometer connected to g_2 , a second balance is made by

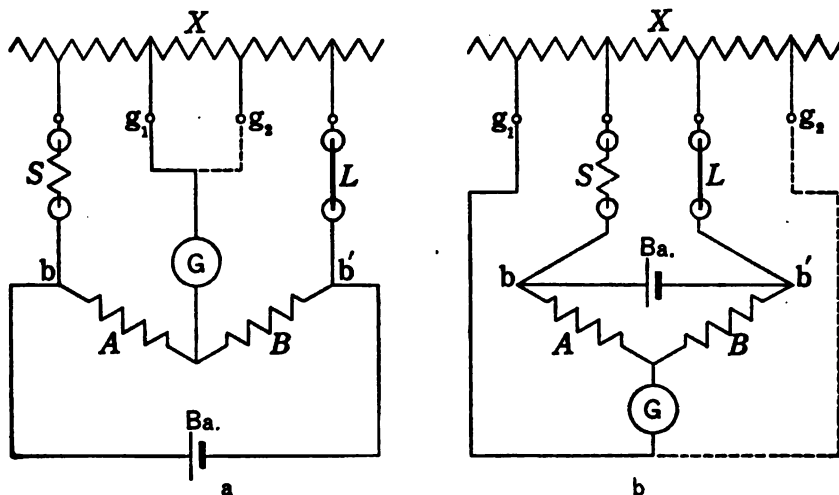


FIG. 3.—Connections for comparing resistances of conductors connected in series by modified Carey-Foster method

an adjustment of A or B . If r is the increase in the value of the ratio of A to B then¹¹ we have

$$X = (S - L) (1 + r) \quad (19)$$

With the connections as shown in Fig. 3*b*

$$X = (S - L) \left(1 + \frac{r}{2} \right) \quad (20)$$

With this latter connection the adjacent 1000 or 100-ohm coil is in the galvanometer circuit. By substituting one coil after another

¹¹ Equations (19) and (20), although not exact, give very accurate results if the coils in the potentiometer are nearly equal to $S - L$ and the connecting resistances are small compared with the resistance of one coil. As the method has been used the errors have seldom amounted to more than 0.001 per cent.

at X various values of r are obtained from which the relative values are directly obtained without an accurate knowledge of the value of $S-L$.

Another method of measuring a number of nearly equal coils connected in series has been used. The connections are as shown in Fig. 4. The bridge is balanced by adjusting A or B , (1) with the battery connected at b_1 and b'_1 , (2) with the battery connected at b_2 and b'_2 , (3) with ratio coils A and B interchanged and the battery connected at b_1 and b'_1 , and (4) with ratio coils as in (3) and battery connected at b_2 and b'_2 . From the observed changes in the ratio of

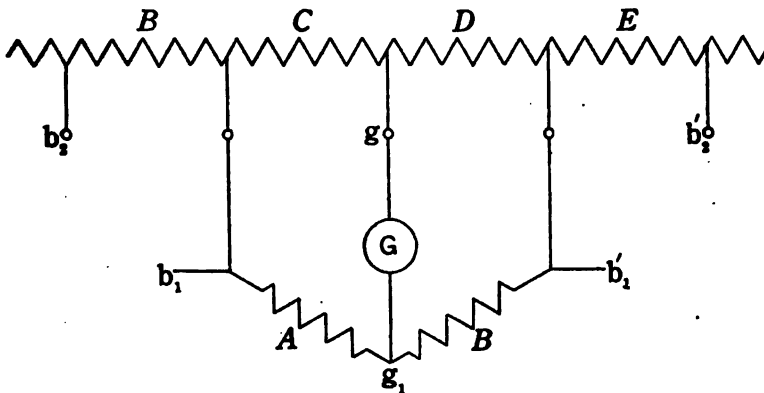


FIG. 4.—Connections for comparing resistances of conductors connected in series by successive ratio method

A to B the ratio of C to D is calculated. In a like manner we obtain the ratio of D to E , E to F , etc., from which the relative values are readily calculated. From such measurements the relative values of all the resistances of the first and second dial may be obtained.

From the relative values or values in ohms of all the resistance sections the corrections a_1 , a_2 , a_3 , a_4 , a_5 , and b may be calculated. In case no standard resistances are used (or the values of the standard resistances are not accurately known) it is generally convenient to proceed with the calculation in the following way:

1. Subtract from the values found for the different sections of the first (or main) dial such a value as will make the mean remain-

der for all approximately zero, or better, the mean remainder for the 10 sections included in R_s equal to zero. This gives a series of corrections to the different sections which are smaller the better the sections are adjusted. The value of R_s when e_1, e_2, e_3, e_4 , and e_5 are each zero is the value of a_1 for $e_1 = 0$. If to this we add the correction to the first section we have the value a_1 for $e_1 = 1000$. If to the value of a_1 for $e_1 = 1000$ we add the corrections to the second section we have the value of a_1 for $e_1 = 2000$. If to this we add the correction to the third section we have the value of a_1 for $e_1 = 3000$. In a like manner the values of a_1 for $e_1 = 4000, 5000, 6000$, etc., are obtained.

2. Subtract from the values found for the different sections of the second dial (including $\Sigma 100$) a value such as will make the sum of the values for those sections used to make up $\Sigma 1000$ equal to the correction found in (1) for $\Sigma 1000$. This gives a series of corrections the first of which is a_2 for $e_2 = 100$; the sum of the first and second is a_2 for $e_2 = 200$; the sum of the first, second, and third is a_2 for $e_2 = 300$, etc. For $e_2 = 0$, a_2 is zero, since the correction for e_2, e_3, e_4 , and e_5 each equal to zero is included in a_1 for $e_1 = 0$.

3. If the value found by measuring $\Sigma 100$ directly is in good agreement with the value found in (2), we may consider that the units of resistance of the bridge and of the potentiometer are substantially equal. In this case the values of a_3, a_4 , and a_5 may be obtained directly by subtracting the corresponding readings of e_3, e_4 , and e_5 from the values of the resistances as measured with the bridge. Care should be taken to see that the value of R_s with e_3, e_4 , and e_5 each equal to zero is first subtracted from the measured values as has been pointed out above. (See p. 13.) In case the value of $\Sigma 100$ as obtained directly with the bridge is not in good agreement with the value as obtained in (2), all values obtained with the bridge should be multiplied by the ratio of the latter to the former before subtracting to obtain a_3, a_4 , and a_5 .

4. Subtract from the values found for the resistance between the highest point on the first dial and the various points on the standard cell dial 183 for $s = 1.0183$, 184 for $s = 1.0184$, 185 for $s = 1.0185$, etc. This gives a series the successive terms of which, when added to the sum of the corrections to the 10 sections of

the first dial which are included in R_s , are corrections pertaining to the corresponding readings of s . Dividing each term by $10\,000 \times s$ and changing the sign gives a series the different terms of which are the values of b corresponding to the readings s .

If 1000 and 100-ohm resistance standards, whose corrections are accurately known, are used we have data which so far we have not considered. This data may be used (a) as a check on the ratio of the mean value of the 1000-ohm sections to the mean value of the 100-ohm sections as determined by use of $\Sigma 1000$ measurement, or (b) to determine the value of resistance of the

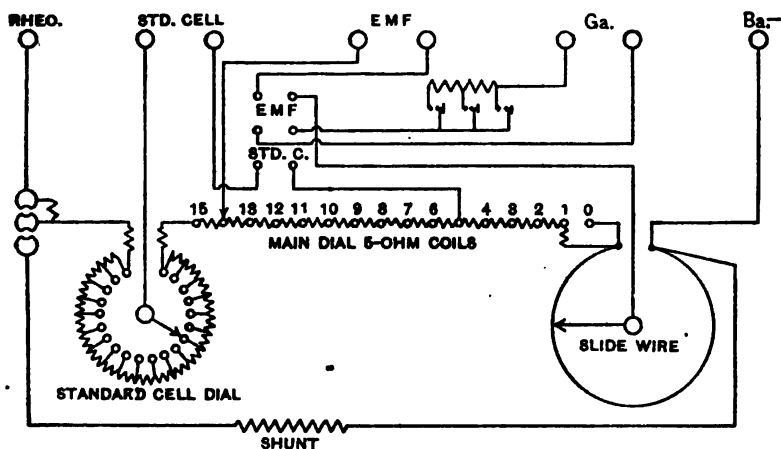


FIG. 5.—Diagram of Leeds and Northrup potentiometer

1000 and 100-ohm sections in ohms. If the values in ohms of the different sections are known, the corrections a_1, a_2, a_3, a_4 , and a_5 are obtained by subtracting the readings e_1, e_2, e_3, e_4 , and e_5 from the values of the corresponding resistances and the correction b is obtained by subtracting from the reading s the value of the resistance R_s and dividing the remainder by $10\,000 \times s$.

As has been pointed out above (p. 8) it is desirable to make the correction b zero for that setting of the standard cell dial most used. The first method outlined above for calculating the corrections usually makes b small while the second may not. It may therefore be desirable to replace this set of corrections by a

new set in which b is zero for $s = 1.0185$ (or some other chosen value). If the new set is $a'_1, a'_2, a'_3, a'_4, a'_5$ and b'

$$b' = b - b_1 \cdot 0.0185 \quad (21)$$

$$\left. \begin{aligned} a'_1 &= a_1 + e_1 b_1 \cdot 0.0185 \\ a'_2 &= a_2 + e_2 b_1 \cdot 0.0185 \\ a'_3 &= a_3 + e_3 b_1 \cdot 0.0185 \\ &\text{etc.}^{12} \end{aligned} \right\} \quad (22)$$

Crompton Type.—A diagram of the connections of a potentiometer of the Crompton type as made by the Leeds & Northrup

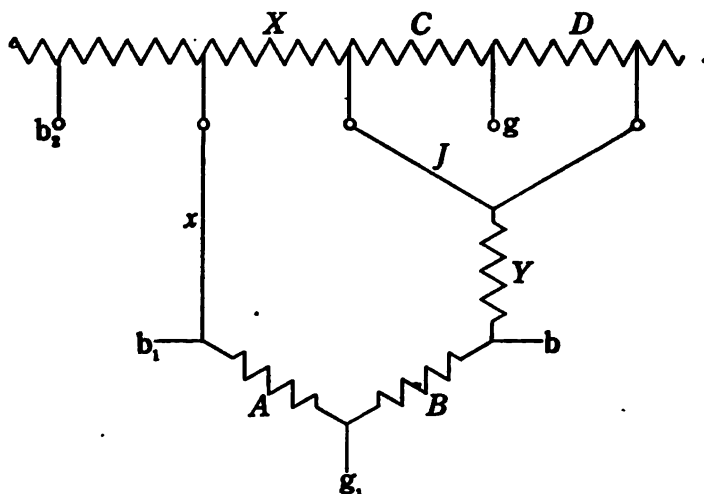


FIG. 6.—Connections for comparing resistances of conductors connected in series by Thomson bridge method

Co. is shown in Fig. 5. Several methods of testing this potentiometer have been used. On account of the low resistance of the coils (5 ohms) the resistances of the posts and connections introduce uncertainties in the measurements when the simple bridge method is used. In order to eliminate errors on account of these resistances a Thomson bridge method has been used. (See Fig. 6.) In the figure A and B represent variable ratio coils and X, C , and D are the approximately equal coils in the potentiometer. Y is an auxiliary resistance about equal to X .

¹² Here b is the old correction for any reading s for which the new correction b' is desired and $b_1 \cdot 0.0185$ is the old correction for $s = 1.0185$.

Since $A/B = X/Y = C/D$ very nearly and J is small we have

$$X + x = AY/B, \text{ very closely.} \quad (23)$$

By shifting the battery connection from b_1 to b_2 and rebalancing, the connecting resistance x can be determined. By substituting one coil after another in the bridge, relative values of the coils are obtained. In this method it is seen that the two adjacent coils are used as the auxiliary ratio coils. The slide wire of this potentiometer can not be measured by this method on account of the high and uncertain resistance of the sliding contact.

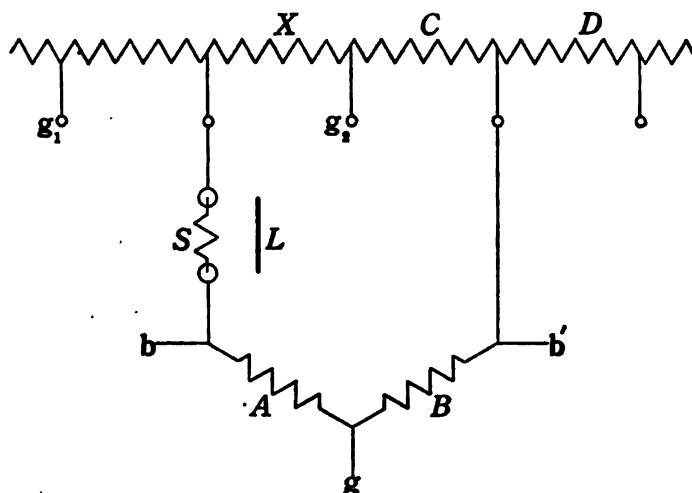


FIG. 7.—Connections for comparing resistances of conductors connected in series by modified Callendar and Griffiths method

The 5-ohm coils have also been measured by means of the modified Carey-Foster method as described on page 14 for the measurement of the 1000 and 100-ohm coils of the Wolff potentiometer.

The successive ratio method, described on page 15, and a modification of the Callendar and Griffiths bridge method have been used to measure the relative values of the 5-ohm coils. The connections for measurement by the latter method are shown in Fig. 7. With a 10-ohm coil at S and the galvanometer connected to g and g_1 a balance is made. The 10-ohm coil is then short-circuited by a conductor of very low resistance L, the galvanometer

connection changed from g_1 to g_2 , and the bridge rebalanced by a change of the ratio of A to B . If $(1 + r_1)$ is the value of this ratio

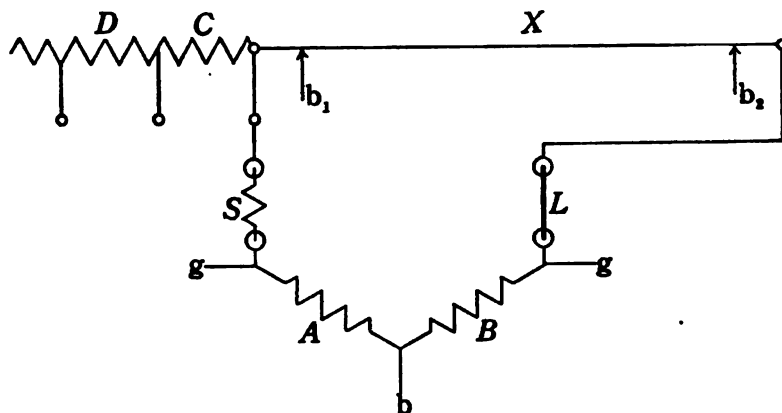


FIG. 8.—Connections for measuring mean resistance per division of slide wire by Carey-Foster method

in the first case and $(1 + r'_1)$ is the value in the second case, where r_1 and r'_1 are both small in comparison with unity, then ¹³

$$X_1 = \frac{(S-L)}{2} \left(1 - r_1 + \frac{r'_1}{2} \right) \quad (24)$$

Likewise from the measurements of the other coils we get

$$X_2 = \frac{(S-L)}{2} \left(1 - r_2 + \frac{r'_2}{2} \right) \quad (25)$$

$$X_3 = \frac{(S-L)}{2} \left(1 - r_3 + \frac{r'_3}{2} \right)$$

Since $\frac{(S-L)}{2}$ is constant these measurements give the relative values of the coils.

The mean resistance per division of the slide wire has been measured by the Carey-Foster method with connections as shown in Fig. 8. This measurement gives two settings on the slide wire between which the resistance is $S - L$. If this difference is the same as that used in the measurement of the coils in the main dial, by

¹³ This equation (24) is not exact, but gives very accurate results if the connections are of low resistance and the coils in the potentiometer are nearly equal in resistance to $1/2 (S-L)$. For example, if none of the coils differ by more than 1/10 per cent from $1/2 (S-L)$ and the resistance of connections is not more than 0.05 ohm, the error introduced by using the approximate formula is less than 1 in 100 000.

the modified Carey-Foster method, the mean resistance per division is obtained on the same basis as are the resistances of the coils in the main dial. In any case, relative values can be obtained by using standard resistances of known values.

Another arrangement is to make two settings 1000 divisions apart on the slide wire and measure the resistance between them by the modified Carey-Foster method described above. This measurement has been regularly made along with the measurement of the 5-ohm coils by the modified Carey-Foster method.

The Callendar and Griffiths method has been used to measure the mean resistance per division of the slide wire. The connections are as shown in Fig. 9. By balancing with the ratio connected first at m and then at n two settings on the slide wire are obtained. Then,

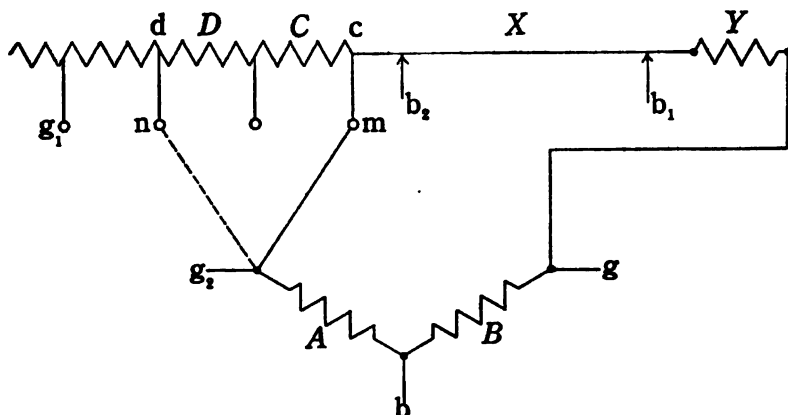


FIG. 9.—Connections for comparing mean resistance per division of slide wire with the resistance of the first two 5-ohm coils of main dial Callendar and Griffiths method

knowing the ratio A/B , the resistance between these two settings is obtained in terms of the first two 5-ohm coils. Therefore this method gives a value of this resistance on the basis on which the values of all the 5-ohm coils are expressed. In this method the use of auxiliary known standards is unnecessary but a resistance of about 5 ohms must be inserted at Y . The resistance A must be considered as including all the resistance from b to c (or d).

That part of this resistance from g_2 to c (or d), although small, is generally unknown. It can, however, be readily measured by changing one of the galvanometer connections from g_1 to g_2 and noting the change in the setting of the slide wire contact necessary to reestablish the balance.

Another arrangement is to make two settings on the slide wire 1000 divisions apart and measure the resistance between them by the modified Callendar and Griffiths method described above. This measurement has been regularly made along with the measurement of the 5-ohm coils by the modified Callendar and Griffiths method.

A modification of the Matthiessen-Hockin method has also been used. A plan of the connections is shown in Fig. 10. Two balances are made, one with the battery connected to *b* and 2, and another at *b'* and 3. The balances are made by adjusting the position of the slide wire contact. Under these conditions the following relation holds:

$$X = (A + a)C/B \quad (26)$$

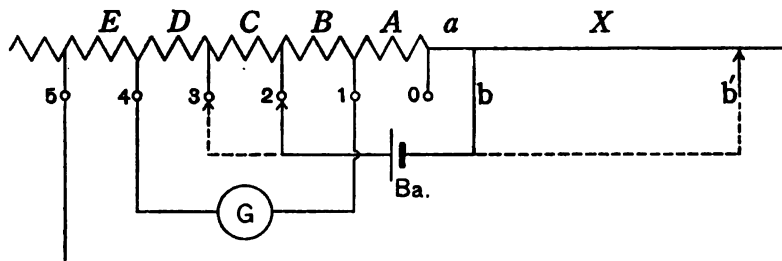


FIG. 10.—Connections for comparing mean resistance per division of slide wire with the resistance of 5-ohm coils of main dial by Matthiessen and Hockin method

From the two readings of the slide wire and the values of the first three 5-ohm coils the mean resistance per division of the slide wire is calculated.

The mean resistance per division of the slide wire can be measured in terms of the first three 5-ohm coils by forming the bridge shown in Fig. 11. Two balances are made by adjustment of the sliding contact.¹⁴ In the first the points *g*₁, *b*, *g*, and *b*₁ are used as branch points and in the second the points *g'*₁, *b'*, *g'*, and *b'*₁ are used. If *X* is the resistance of the slide wire between the two points at which the sliding contact must be set to establish the two balances of the bridge, then

$$X = AC/B \quad (27)$$

very exactly, if *A*, *B*, and *C* are nearly equal.

¹⁴ Wenner: *Phys. Rev.*, 17, p. 384; 1903.

Three 10-ohm resistance standards have also been used in conjunction with the slide wire and the first two 5-ohm coils of the potentiometer, as shown in Fig. 12, where B , C , and n represent the

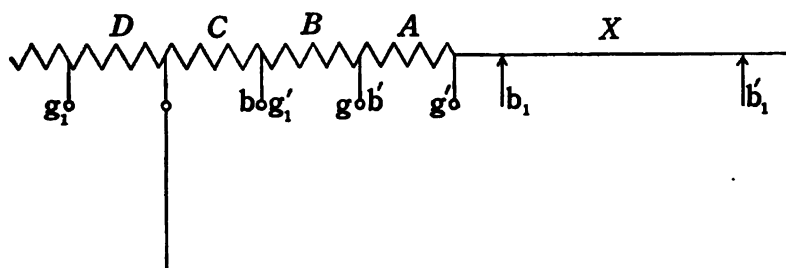


FIG. 11.—Connection for comparing mean resistance per division of slide wire with the resistance of the first three 5-ohm coils of the main dial

10-ohm resistance standards. This arrangement is a combination of the Matthiessen-Hockin and Thomson bridges and gives

$$X = (A + a)C/B \quad (28)$$

The resistance r need not be known but should be between 0.1 and 0.9 ohm so as to give suitable settings on the slide wire. The

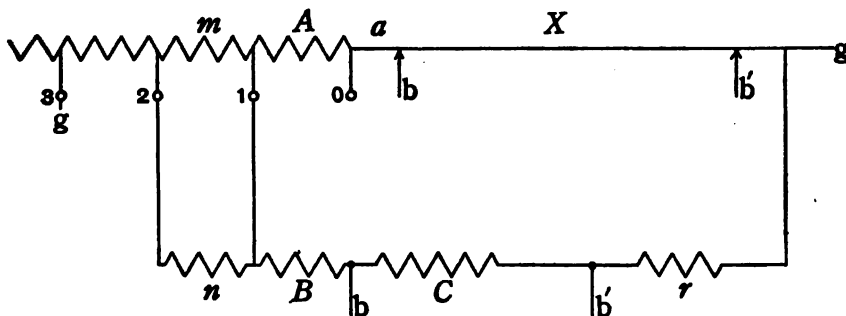


FIG. 12.—Connection for comparing mean resistance per division of slide wire with that of first 5-ohm coil of the main dial using three nearly equal standard resistances

error which would otherwise be introduced on account of the resistance of the connection between A and B is made negligibly small by using the coils m and n as shown.

The calibration of the slide wire of a potentiometer of the Crompton type may be made by several different methods. In the Carey-Foster the Strouhal and Barus,¹⁵ and possibly some

¹⁵ Bull., U. S. Geol. Sur., 14; 1885.

other methods the resistance or relative values of the resistance of short sections of the wire are measured. The calibration correction, therefore, at any point near the center depends upon a number of settings and readings in such a manner that its probable error is several times the probable error of a single setting and reading. Since we try to make the calibration to an accuracy as high as can be attained in the setting and reading of positions of the slide-wire contact such methods have not been used.

With suitable apparatus the Matthiessen and Hockin method is not only more convenient than the methods mentioned above but by its use the calibration corrections can be obtained to the

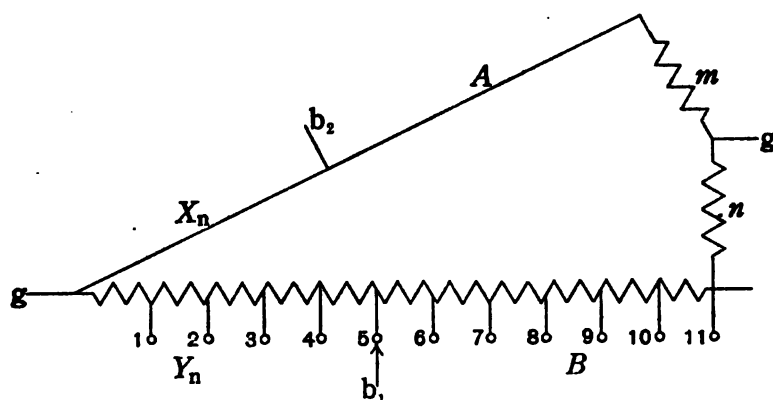


FIG. 13.—Arrangement for calibrating slide wire by Matthiessen and Hockin method using coils of main dial

accuracy attainable in setting and reading the positions of the sliding contact. The Matthiessen and Hockin method has therefore been regularly used in the calibration of the slide wire of potentiometers of the Crompton type. Connections as shown in Fig. 13 have been used in calibrating at 11 points the slide wires of Leeds and Northrup potentiometers. A simple Wheatstone bridge is made up of the first eleven 5-ohm coils, the slide wire and two resistances m and n . This bridge is balanced by the adjustment of the position of the slide-wire contact, to which one battery terminal is connected, with the other battery terminal connected successively to the different branch points between the 5-ohm coils.

Each of the balances gives

$$\frac{X_n}{Y_n} = \frac{A+m}{B+n} = \frac{A+m+X_n}{B+n+Y_n} \quad (29)$$

where X_n is the resistance of the slide wire between the zero end and the point at which the contact is set and Y_n is the resistance of the series of 5-ohm coils between the terminal g and the contact b_n . Since $A+m+X_n$ and $B+n+Y_n$ are constant

$$X_n = k Y_n, X_1 = k Y_1, X_2 = k Y_2, X_3 = k Y_3, \text{ etc.} \quad (30)$$

Since we know the relative values of the 5-ohm coils we can calculate the relative values of Y_1, Y_2, Y_3 , etc. These are the relative values of the resistances of the slide wire corresponding to the various settings at which balances were made. By a preliminary adjustment of the resistances m and n these settings can be made to occur at points on the slide wire at which corrections are desired.

The calibration obtained by this method depends upon the accuracy of the setting and reading of the position of the slide wire contact and the accuracy to which the relative values of the 5-ohm coils are known. As the latter are regularly determined to an accuracy higher than the former can be made, the error in the calibration at any point at which a balance is made is approximately the error in the setting and reading at this point. In order to calibrate the slide wire at 22 points, it is only necessary to use 12 coils instead of 11 and arrange a 10-ohm resistance so that it can be made to shunt any two adjacent coils. By balancing the bridge, using the junction of the two coils as a branch point, the 5 ohms is halved, so that changes of $2\frac{1}{2}$ ohms are obtained.

In the Leeds and Northrup potentiometer the standard cell is balanced across a resistance consisting of 10 of the 5-ohm coils in the main dial, an odd-valued coil and the coils in the standard cell dial. The measurement of the 5-ohm coils has been considered above. The odd-valued coil and the coils in the standard cell dial are measured by using the potentiometer connected, as shown in Fig. 14. The bridge so formed is balanced for all settings of the standard cell dial by adjusting the contact on the slide wire. A

¹⁴ In the calculation it is necessary to assume that the points 1 and 1₄ are at the same potential. These points are, therefore, connected together by a conductor of low resistance. Also one battery connection, *g*, is made at such a point on the connection (having a resistance of about 0.1 ohm) between the Rheo, and Ba—terminals as will bring the balance point on the slide wire very near the zero end when one terminal of the galvanometer is connected at 1₅ instead of b₂. In addition, the other battery connection, *g'*, is made to both points 7 and 8. With this arrangement, one step on the standard cell dial corresponds to one numbered division on the slide wire, but the corrections as determined depend upon several readings of the slide wire, among them some of those used in the calibration of the slide wire. The accuracy, therefore, is not as good as is sometimes desired.

ratio of R to S has been measured by a bridge method, and the factor calculated. In measuring this ratio extreme care must be taken, otherwise errors are introduced on account of connecting resistances. Where the reduction factor is nominally 0.1, R/S should equal 1/9 and the compensation resistance 0.9 R . In this case the reading f may have a value of either 1 or 0.1. In stating the corrections the correction d is taken as zero for $f=1$, therefore for $f=0.1$,

$$d = 10 S / (R + S) - 1 \quad (31)$$

In "split-circuit" or divided-circuit potentiometers, if provision is made for opening the parallel circuits, the relative values (or values in ohms) of the resistance sections may be determined by one or another of the methods described above. With the relative values known the corrections can be determined, though the calculations are often much more complicated than for potentiometers of the Feussner or Crompton type.

From what has been said it will be evident that the work involved in making the measurements and calculations necessary for determining the corrections to a potentiometer by any of the methods already considered is by no means small. As the Bureau of Standards is called upon to test a number of potentiometers each year it seemed desirable, in order to reduce the time required for making a test, to use a more direct method even though to do so might require the construction of special apparatus and some sacrifice as to accuracy. In any direct method the results obtained depend not only upon the measurements made but also directly upon the calibration of the apparatus used in making the test. Therefore, in general, the results can not be as accurate as those obtained by the methods discussed above.

4. RATIO-SET

A consideration of the matter led to the conclusion that the Matthiessen-Hockin method, with suitable apparatus, would give an accuracy sufficient for most of the tests, would result in a material saving of time in making the measurements, and could be made to give the data in such form that the calculation of the corrections would require but a small amount of time. It should

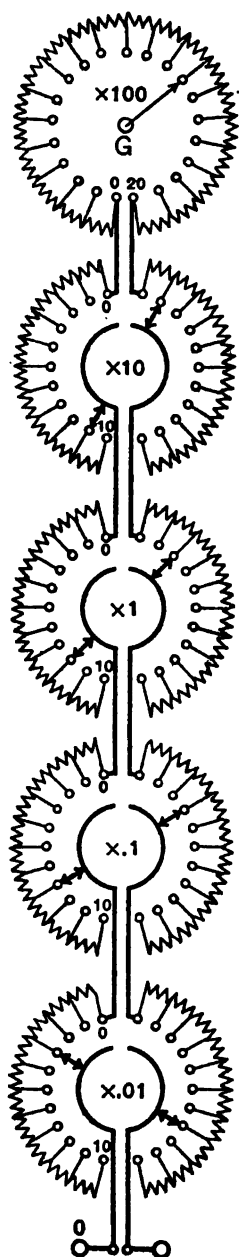


FIG. 15.—Diagram of connections of ratio-set

also be mentioned that according to this method a test can be made with a potentiometer under practically operating conditions. Accordingly, apparatus which we designate as a ratio-set was designed for use according to this method. The apparatus was constructed by O. Wolff, of Berlin, and delivered to the Bureau of Standards in the summer of 1912. It has been found very satisfactory not only in the testing of potentiometers but in general use in resistance measurements.

(A) DESCRIPTION

The ratio-set is made up of 100 resistance coils connected as shown in Fig. 15. It will be seen that it is equivalent to a long slide wire having a resistance of 2111.1 ohms and upon which contact can be made at intervals of 0.01 ohm. The resistance between the zero and the unmarked binding post is 2111.1 ohms and is independent of the settings of the dials while the resistance between the zero terminal and the galvanometer terminal (G) is variable in steps of 0.01 ohm from 0 to 2111.1 ohms. The resistance coils are made of manganin wire and excepting the 0.1 and 0.01-ohm sections are wound in a single layer on metal tubes. The 0.1 and 0.01-ohm sections, being made from short thick wires, require no special supports.

The four double dials are similar to the 10, 1, and 0.1-ohm dials of the Wolff potentiometer except that the usual screws for making independent connection to the terminal blocks are replaced by tapered holes. The 100-ohm dial is a simple one by means of which the galvanometer can be connected to either terminal of any 100-ohm coil. All of the dial switches are provided with clicking devices

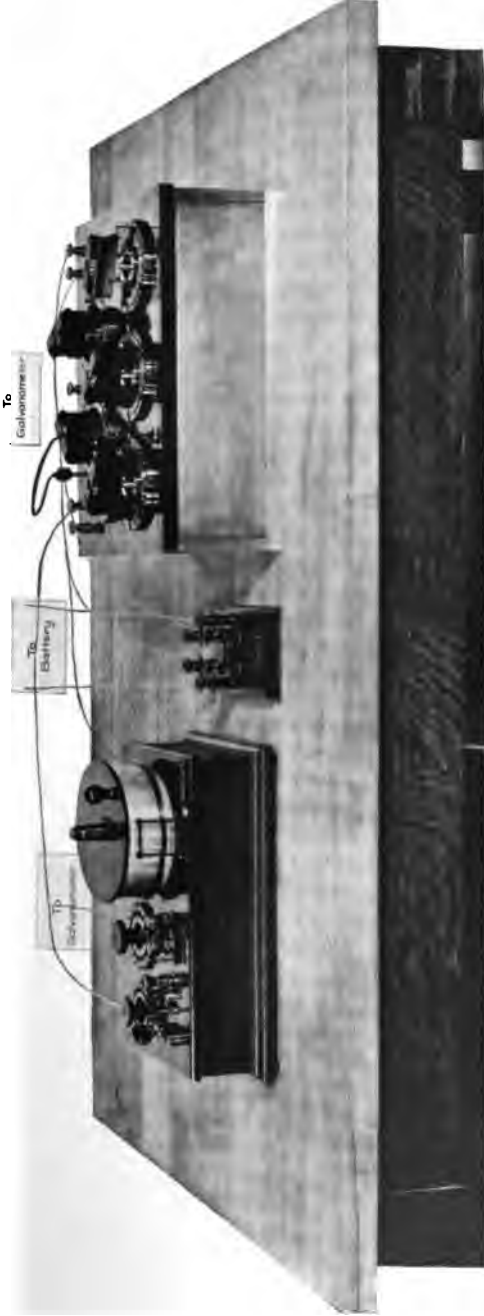


FIG. 16.—Ratio-set connected to Leeds and Northrup potentiometer as used in testing the potentiometer

to indicate the proper positions. In Fig. 16 the ratio-set is shown connected to a Leeds and Northrup potentiometer as it is used in calibrating the potentiometer.

(B) CALIBRATION

In order to obtain the complete calibration of the ratio-set the following measurements were necessary: (a) total resistance for all settings, (b) resistance between the zero and the galvanometer branch point for all settings, and (c) temperature coefficients of the coils.

The total resistance was measured by a simple Wheatstone bridge method and was found to be practically independent of the settings of the dial switches. The maximum variation was 0.0014 ohm or 7 parts in 10 000 000 of the total resistance. Variations due to changes in switch contact resistances amounted to 0.0001 ohm. The resistance between the zero and the galvanometer branch point for all settings was obtained by measuring it when the setting was zero and adding to this the measured changes produced on changing the switches. In the 100-ohm dial these changes are the actual resistances of the coils between branch points, but in the other dials the changes are the actual resistances between branch points plus any changes due to changes in the connections to the coils.

The 100-ohm coils were measured by the modified Carey-Foster method. The connections were made as shown in Fig. 3a. By this method the resistance between the post junctions is measured in terms of a standard resistance. This is the resistance required, since the posts are in the galvanometer circuit. The 10, 1, and 0.1-ohm coils were measured by a substitution method, using connections as shown in Fig. 17. With the switch as shown and the galvanometer connected to g_1 , the bridge is balanced by adjusting the ratio A/B . The resistance in the left arm is $S + p + c$

where S is the resistance of the standard,
 p is the resistance of the ppst,
and c is the resistance of the connections.

Now the switch is shifted to the dotted position, the standard resistance short-circuited by or interchanged with the link L ,

and the galvanometer changed to g_1 . Suppose the ratio must be increased an amount r in proportional parts in order to restore the balance of the bridge. The resistance in the right arm is now

$$L + X + p' + c$$

where L is the resistance of the short-circuiting link,
 p' is the resistance of the post,
 X is the resistance of the coil,
 and c is the connecting resistance assumed to be the same as before.

From the two balances of the bridge we have

$$(L + X + p' + c) = (S + p + c) (1 + r) \quad (32)$$

and since L , p , and c are small in comparison with X and s , and r is small in comparison with unity,

$$X + p' - p = (S - L) (1 + r) \quad (33)$$

approximately. Since $X + p' - p$ is the amount by which the resistance controlled by the switch is increased on changing the switch from g_2 to g_1 , this method gives the resistance with which we are concerned in the use of the apparatus.

In the calibration an effort is made to get the corrections to 0.001 ohm or 0.1 step on the lowest dial. If care is taken, this accuracy can be obtained with a good quality bridge in measurements of 1 ohm and less. The 0.01-ohm coils (or sections) were and the 0.1-ohm coils might have been measured by connecting the center (or G) and o-terminal to the X-terminals of the bridge, and measuring the resistances corresponding to all possible readings of the 0.01-ohm dial, with the other dials so set that none of the other resistances coils are included in the resistance measured. By this procedure also the measured resistances include any differences there may be in the resistances of the connections to the coils.

From the calibration of the ratio-set we get the resistance between the o and G posts (branch points to battery and galvanometer) for any reading of the ratio-set. However, as used it is

only the relative values of these resistances that is required, so a unit is chosen which makes the corrections much smaller than the corrections necessary to give the values in ohms. For convenience in use a table has been constructed which gives the small correction which must be added to any reading to give the corresponding relative value of the resistance which we designate as A .

The temperature coefficients of the coils were obtained by repeating the calibration with the apparatus at another tempera-

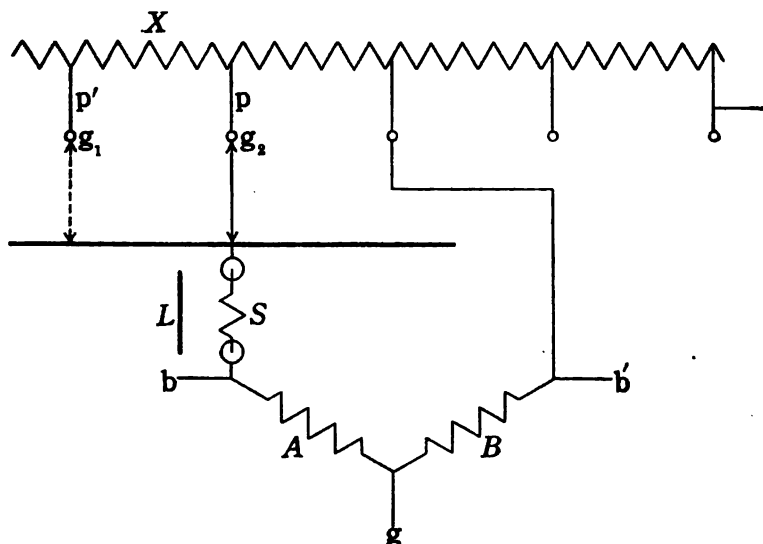


FIG. 17.—Arrangement for measuring change in resistance corresponding to steps of a dial switch of the ratio-set

ture. From the two measurements it was found that the temperature coefficients of the 100-ohm coils were very nearly equal, the greatest difference from the mean being 0.0002 per cent per degree centigrade. Since only relative resistances are required this would cause an error less than 0.000002×10 or 2 in 100 000 at a temperature differing 10° C. from that at which the corrections were determined.

(C) USE IN TESTING POTENTIOMETERS

To use the ratio-set in the calibration of a potentiometer connections are made as shown in Fig. 18. This gives us a Wheatstone bridge, two arms of which are formed by the ratio-set $o G t$ and the other two by the potentiometer $l m n o p q$ and its external resistance R . Suppose that the correction to the reading e is required, assuming that when the potentiometer is in use the known electromotive force is balanced when the reading was s . The potentiometer is set so that the reading is s and the bridge $o o t G$ balanced by adjusting the dial switches of the ratio-set. Let the resistance A of the ratio-set be A_s . Now by balancing the bridge $o p t G$ (i. e., with one galvanometer connection changed from o to p) we get A'_s . These give

$$\frac{R_s}{A'_s - A_s} = \frac{1}{k} \quad (34)$$

where k is the ratio of the current through the potentiometer to that through the ratio-set. Let the

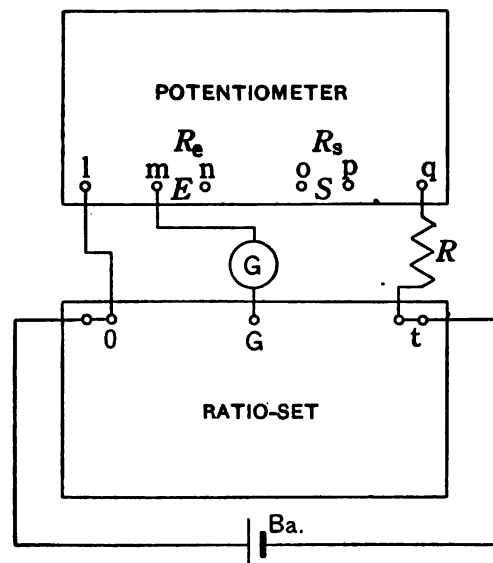


FIG. 18.—Connections for calibrating any potentiometer by means of the ratio-set

potentiometer be set now so that its reading is e and two more balances made, first using $o m t$ and G as branch points and then using $o n t$ and G . Let the corresponding values of A be A_o and A'_o . Then

$$\frac{R_o}{A'_o - A_o} = \frac{1}{k'} \quad (35)$$

from which it follows that

$$\frac{R_o k'}{R_s k} = \frac{A'_o - A_o}{A'_s - A_s} \quad (36)$$

But $\frac{k'}{k} = \frac{I'}{I}$ of equation (2) since R is the external resistance as actually used. Therefore

$$\frac{E}{S} = \frac{A'_s - A_s}{A'_s - A_s} \quad (37)$$

from which the correction to the reading can be calculated if S is known. If the potentiometer is compensated $I'/I = 1$ and is independent of the resistance R so that R may be chosen arbitrarily. It should be noticed that this is the Matthiessen-Hockin method of comparing R_s with R_s .

From equations(11) and (37) we get that

$$\frac{E}{S} = \frac{f}{s} (1 + b + d) (e + a) = \frac{A'_e - A_e}{A'_s - A_s} \quad (38)$$

Since we wish to have b zero for $s = 1.0185$ and d zero for the normal range ($f = f_0$) we get by substitution

$$\frac{f_0(e + a)}{1.0185} = \frac{A'_e - A_e}{A'_{1.0185} - A_{1.0185}}$$

from which

$$a = \frac{1}{f_0} \frac{(A'_e - A_e) 1.0185}{(A'_{1.0185} - A_{1.0185})} - e \quad (39)$$

By substituting this in equation (38) we get when we put $f = f_0$ and $d = 0$

$$b = 1 - \frac{1.0185}{(A'_{1.0185} - A_{1.0185})} \frac{A'_s - A_s}{s} \quad (40)$$

The correction d can be determined for any range by setting $e = e'$ any convenient large value, $s = 1.0185$ and $f =$ the reading of the range switch for which the correction is to be determined and making four more balances. These give the four resistances $\bar{A}_e$, $\bar{A}'_e$, $\bar{A}_{1.0185}$ and $\bar{A}'_{1.0185}$ and by substitution in (38) we obtain

$$\frac{f}{1.0185} (1 + d) (e' + a') = \frac{\bar{A}'_e - \bar{A}_e}{\bar{A}'_{1.0185} - \bar{A}_{1.0185}} \quad (41)$$

Now from equation (39) we see that

$$e' + a' = \frac{1}{f_0} \frac{(A'_{e'} - A_{e'}) 1.0185}{(A'_{1.0185} - A_{1.0185})} \quad (42)$$

which when substituted in (41) gives

$$d = \frac{(\bar{A}'_{e'} - \bar{A}_{e'})}{(A'_{e'} - A_{e'})} \frac{(A'_{1.0185} - A_{1.0185})}{(\bar{A}'_{1.0185} - \bar{A}_{1.0185})} \frac{f_0}{f} - 1 \quad (43)$$

Equations (39), (40), and (43) give all of the corrections to the potentiometer in terms of the resistances in the ratio-set which are known from its readings and its corrections.

The calibration of potentiometers of the Crompton type is comparatively easy. The total resistance is constant, the dials are independent, and, further, the resistance between one end of the potentiometer and any potential terminal is dependent on the setting of only one dial. Therefore the total number of balances necessary is of the same order as the total number of points on the dial and points on the slide wire for which corrections are to be determined. From the preceding discussion it will be seen that if

$$A'_{1.0185} - A_{1.0185} = u(1.0185) \quad (44)$$

where u is approximately a decimal multiple or submultiple of ten the calculations are simplified. In case of the Leeds and Northrup potentiometer it is convenient to make $u = 1000$. This gives

$$a = \frac{A'_{e'} - A_{e'}}{1000} - e \quad (45)$$

$$b = s - \frac{A'_{s'} - A_{s'}}{1000} \text{ approximately} \quad (46)$$

and ¹⁷

$$d = \frac{\bar{A}'_{e'} - \bar{A}_{e'}}{A'_{e'} - A_{e'}} \frac{1}{f} - 1 \quad (47)$$

On the data sheet is given a complete record of the calibration of a Leeds and Northrup potentiometer for all readings of the standard

¹⁷ Equation (47) differs from equation (43), since in the use of the potentiometer with $f=0.1$ (or 0.01) the standard cell is regularly balanced with $f=1$, so that $A'_{1.0185} - A_{1.0185} = \bar{A}'_{1.0185} - \bar{A}_{1.0185}$.

DATA SHEET FOR CALIBRATION OF LEEDS AND NORTHRUP
POTENTIOMETER No. 6082

	Pot'meter reading	Ratio set readings at—		Relative resistances			Correction
	s	o	p	A _s	A' _s	A' _s - A _s	b
STANDARD CELL DIAL	1.0185	80.08	1098.58	80.80	1098.58	1018.50	±0.00000
	1.0175	80.98		80.98		1017.60	— .00010
	6	.89		.89		.69	— .00009
	7	.80		.80		.78	—
	8	.70		.70		.88	—
	9	.61		.61		.97	—
	1.0180	.52		.52		1018.06	—
	1	.43		.43		.15	—
	2	.34		.34		.24	—
	3	.25		.25		.33	—
	4	.17		.17		.41	—
	5	.08		.08		1018.50	± .00000
	6	79.98		79.98		.60	±
	7	.88		.88		.70	±
	8	.78		.78		.80	±
	9	.69		.69		.89	±
	1.0190	.60		.60		.98	±
	1	.50		.50		1019.08	±
	2	.41		.41		.17	±
	3	.32		.32		.26	±
	4	.22	1098.58	.22	1098.58	.36	±
MAIN DIAL	o	m	n	A _s	A' _s	A' _s - A _s	a
	0.00000	1598.56	1598.58	1598.57	1598.59	0.02	+0.00002
	.1	1498.58		1498.58	1598.59	100.01	+
	.2	1398.59		1398.59		200.00	±
	.3	1298.59		1298.59		300.00	±
	.4	1198.58		1198.58		400.01	+
	.5	1098.58		1098.58		500.01	+
	.6	998.57		998.58		600.01	+
	.7	898.57		898.57		700.02	+
	.8	798.57		798.57		800.02	+
	.9	698.56		698.56		900.03	+
	1.0	598.55		598.55		1000.04	+
	1.1	498.54		498.54		1100.05	+
	1.2	398.53		398.53		1200.06	+
	1.3	298.52		298.52		1300.07	+
	1.4	198.50		198.50		1400.09	+
	1.5	98.48	1598.58	98.49	1598.59	1500.10	+
SLIDE WIRE	s	o	p	A _s	A' _s	A' _s - A _s	b
	1.0185	80.08	1098.58	80.08	1098.58	1018.50	+0.00000
	o	m	n	A _s	A' _s	A' _s - A _s	a
	0.00000	1598.56	1598.58	1598.57	1598.59	0.02	+0.00002
	.01	1598.56	1608.57	1598.57	1608.57	10.00	±
	.02		1618.57		1618.57	20.00	±
	.03		1628.59		1628.59	30.02	+
	.04		1638.61		1638.61	40.04	+
	.05		1648.61		1648.61	50.04	+
	.06		1658.59		1658.59	60.02	+
	.07		1668.60		1668.60	70.03	+
	.08		1678.61		1678.61	80.04	+
	.09		1688.62		1688.63	90.06	+
	.10	1598.56	1698.60	1598.57	1698.61	100.04	+

Factor plug changed, f=.1

e'	m	n	A _s '	A' _s '	A' _s ' - A _s '	d
1.50000	1538.55 ₈	1688.63 ₈	1538.55 ₈	1688.63 ₈	150.07 ₁	+0.0004 ₈

Date, June 2, 1914.

Temperature, 26.4° C.

cell dial, all readings of the main dial, for 11 points on the slide wire and for both readings of the range plug. The connections used in making this test were as shown in Fig. 19. To make $u = 1000$ four of the 100-ohm sections of the ratio-set were short-circuited and a resistance of about 0.555 ohm placed in series with the potentiometer. This series resistance was easily adjusted so as to make $u = 1000.00$. The measurements then consisted in setting the switches of the ratio-set so as to balance the bridge with the potentiometer set at the readings for which corrections were desired. The calculations indicated by equations (45), (46), and (47) are of such a simple nature that the corrections were obtained

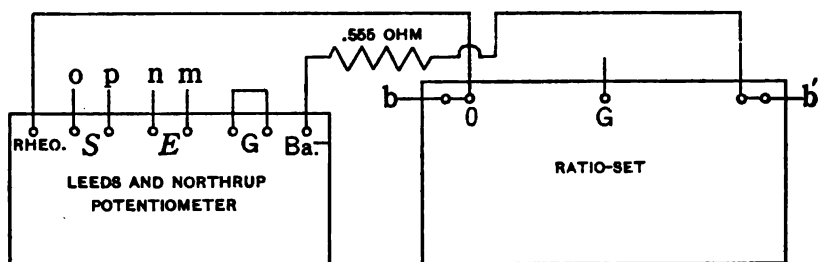


FIG. 19.—Ratio-set connected to Leeds and Northrup potentiometer for calibrating the potentiometer. The arrangement is such that the corrections are obtained from the readings of the ratio-set with but very little calculation.

by inspection, comparing the readings with the corresponding relative resistances.

It remains to divide the reading e and the correction a in two parts as pointed out on page 8. When this is done we have the values of a_1 , b , and d for all readings e_1 , s , and f ; and the values of a_2 for 11 readings e_2 . The values of a_2 for other readings e_2 may be obtained by interpolation. We then have all the correction terms of equation (16) except c which is known from the reading s and the known electromotive force of the standard cell.

In the calibration of the Wolff potentiometer, the total resistance is first measured at the various settings of the dial switches to ascertain whether the potentiometer is compensated. This is done by short-circuiting the 100 and 1000-ohm coils and measuring the resistance of the three lower dials in a Wheatstone bridge.

As the resistance measured is less than 1 per cent of the total resistance the accuracy required in this measurement is not high. The calibration is then carried out in much the same way as for the Leeds and Northrup potentiometer. The connections used are shown in Fig. 20. In this case to obtain the corrections most directly from the readings we make $A'_{1.0185} - A_{1.0185} = 1018.5$, and since $R_{1.0185} = 10185$ the ratio of resistances is 1 to 10, approximately. To make the currents have the desired ratio, auxiliary resistances of 290 and 821 ohms are used as shown. The observations are

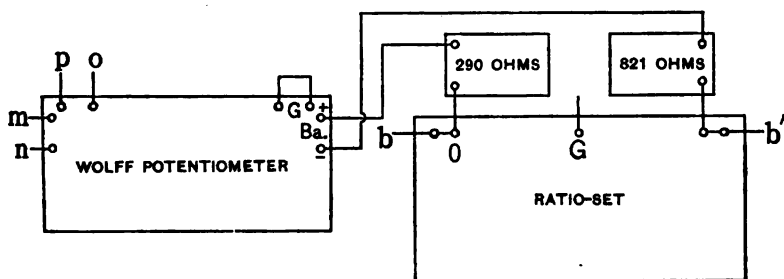


FIG. 20.—Ratio-set connected to Wolff potentiometer. The arrangement is such that the corrections to the potentiometer may be obtained from the readings of the ratio-set by inspection

made and the results tabulated in the same manner as was done for the Leeds and Northrup potentiometer.

To calibrate one of the older Wolff potentiometers which does not have a standard cell dial the procedure is approximately the same as that just given, fewer observations being necessary in this case. Here b , the correction to the standard cell dial reading, is calculated from the corrections to the reading e by use of the relation

$$b = -\frac{a_s}{e_s} \quad (48)$$

shown in the discussion of the theory of the potentiometer (equation 18). The arrangement for testing of other kinds of potentiometers readily suggest themselves, and it will be seen that any normal-range potentiometer can be completely calibrated by means of the ratio-set if the maximum resistance in the potentiometer between two potential terminals is less than twice the re-

sistance across which the known electromotive force is balanced. By a normal-range potentiometer is meant one in which the steps on the first dial correspond to tenths of a volt. In these cases 100 ohms of the ratio-set can be made to correspond to one step

of the first dial, and since there is a hundredth-ohm dial, the reading can be made directly to 0.00001 volt, which is sufficient for most purposes. However, with a good galvanometer, one can interpolate to 0.001 ohm, the ratio-set having been calibrated to this accuracy.

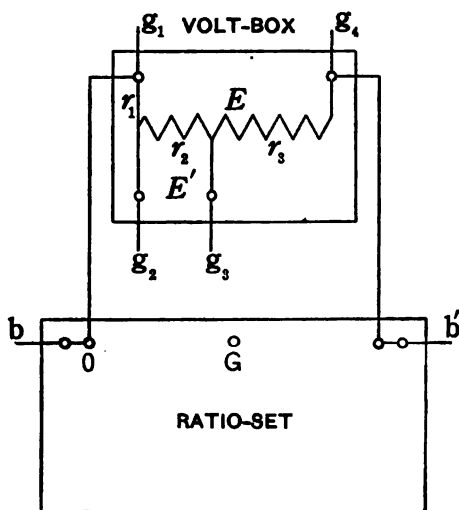


FIG. 21.—Connections for determining factor (or ratio) of volt-box or potential-divider by means of ratio-set

or voltages above $1\frac{1}{2}$ or 2 volts. In use the terminals (see Fig. 21) g_1 and g_4 are connected to the voltage E to be measured while the g_2 and g_3 are connected to the E -terminals of the potentiometer. If E' is the voltage across the E -terminals of the potentiometer and $f(1+d)$ is the factor of the volt box

$$E = E'f(1+d). \quad (49)$$

From the figure it will be evident that

$$f(1+d) = \frac{r_1 + r_2 + r_3}{r_2} \quad (50)$$

or

$$d = \frac{A_4 - A_1}{f(A_3 - A_2)} - 1 \quad (51)$$

where f is the nominal value or reading of the volt-box factor and

(D) OTHER USES

Volt boxes or potential dividers are used in connection with potentiometers for measuring electromotive forces or voltages above $1\frac{1}{2}$ or 2 volts. In use the terminals

A_1 , A_2 , A_3 , and A_4 are relative resistances of the ratio-set when the bridge is balanced successively with the galvanometer connected to g_1 , g_2 , g_3 , and g_4 .

The ratio-set is very useful in measuring resistances to which connections can not be made except through other resistances.

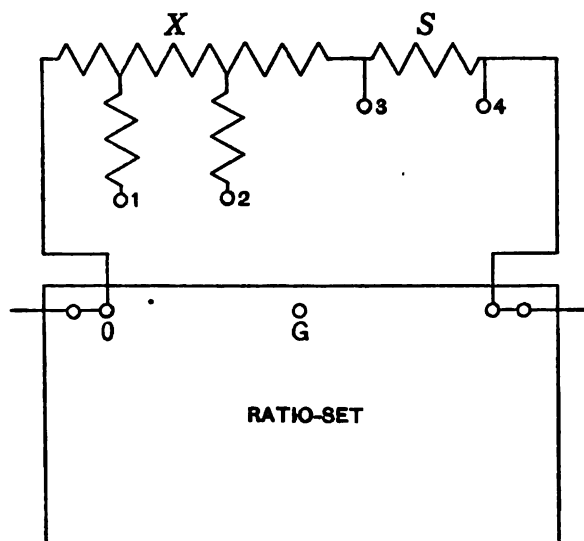


FIG. 22.—Arrangement for measuring resistances to which connection can be made only through other resistances or resistance of four-terminal conductor by means of ratio-set

The connections are made as shown in Fig. 22. By balancing at the four potential terminals we get the relation

$$X = \frac{A_2 - A_1}{A_4 - A_3} S, \quad (52)$$

which gives the unknown resistance in terms of the ratio of the differences in readings of the ratio-set and the value of the known resistance, S .

5. SUMMARY

1. An analysis is made of the relation between the readings of any potentiometer and the ratio of the known and unknown electromotive force.

2. A convenient way of stating the corrections to the readings of a potentiometer of good design and construction is given.

3. Methods of determining these corrections by resistance measurements are described.

4. A device for use in the calibration of potentiometers is described and the method of using it explained and illustrated.

WASHINGTON, June 10, 1914.

THE EMISSIVITY OF METALS AND OXIDES

I. NICKEL OXIDE (NiO) IN THE RANGE 600° TO 1300° C

By G. K. Burgess and P. D. Foote

INTRODUCTION

This paper is the first of a series it is hoped to present on the monochromatic and total radiation of oxides and metals. In addition to whatever scientific interest these results may possess, it is believed that the determination of the radiation properties at high temperatures of some of these substances will be of considerable use in technical applications; for example, providing the necessary corrections to apply to the temperature readings of the various types of optical and radiation pyrometers when sighted upon such materials.

HISTORICAL.—Only a few of the recent papers will be mentioned. Waidner and Burgess,¹ Mendenhall,² and Spence³ have determined the departure of the red radiation of platinum at high temperatures from that of a black body, and Henning⁴ has investigated the radiation of this and other metals, spectropyrometrically, over the visible spectrum. The dispersion of the emissivity of solid and liquid gold has been determined in the visible spectrum by Stubbs and Prideaux,⁵ and of solid and liquid copper and liquid silver by Stubbs.⁶ Tungsten, tantalum, and molybdenum have been studied by Mendenhall and Forsythe⁷; platinum, palladium,

¹ Waidner and Burgess, Bur. Standards Scientific Paper No. 55, 46 pp.; also Burgess, Scientific Paper 24, 3 pp.

² Mendenhall, *Astrophys. J.*, **23**, pp. 91-97; 1911.

³ Spence, *Astrophys. J.*, **27**, pp. 194-197; 1913.

⁴ Henning, *Zs. Instrk.*, **30**, pp. 61-75; 1910.

⁵ Stubbs and Prideaux, *Roy. Soc. Proc. (A)*, **87**, pp. 451-465; 1912.

⁶ Stubbs, *Roy. Soc. Proc. (A)*, **88**, pp. 195-205; 1913.

⁷ Mendenhall and Forsythe, *Astrophys. J.*, **27**, pp. 380-390; 1913.

and tantalum by McCauley⁸; carbon, tantalum, and tungsten, chiefly from a theoretical standpoint, by Hyde⁹; tantalum, and tungsten by Waidner and Burgess¹⁰; and iron by Bidwell.¹¹ Coblentz¹² has investigated spectrophotometrically the radiating properties of a number of metals and oxides, mainly in the infra-red. The total emissivity of molten iron and copper has been observed by Thwing,¹³ and of copper by Burgess.¹⁴ Randolph and Overholser¹⁵ have studied the total radiation of various substances up to 600° C and Langmuir¹⁶ of several materials up to 400–600° C.

OBJECT OF THE PRESENT PAPER.—The object of the present investigation has been the determination of the monochromatic and total emissivity of nickel oxide (NiO). This oxide forms in a tough, smooth layer on the surface of nickel when subjected to high temperatures in an oxidizing atmosphere such as air. The total emissivity of NiO and the monochromatic emissivity and its dispersion in the visible spectrum have been measured for several temperatures in the range 600° to 1300° C.

MONOCHROMATIC EMISSIVITY OF NICKEL OXIDE

METHODS OF MEASUREMENT.—Two methods were employed in the determination of the emissivity of NiO for red light, a preliminary method of microscopic melts and a more exact method of direct comparison by a spectrophotometer of the intensity of light emitted by the glowing NiO and by a black body at the same temperature.

METHOD OF MICROSCOPIC MELTS.—Burgess¹⁷ has found that microscopic samples of various substances show sharp and well-defined melting points when placed on a strip of iridium, platinum, or other suitable metal, electrically heated. Such a microscopic specimen readily takes up the temperature of the strip with prac-

⁸ McCauley, *Astrophys. J.*, **37**, pp. 164–182; 1913.

⁹ Hyde, *Astrophys. J.*, **36**, pp. 89–132; 1912.

¹⁰ Waidner and Burgess, *J. de Physique (4)*, **6**, pp. 830–834; 1907.

¹¹ Bidwell, *Phys. Rev. (2)*, **1**, pp. 482–483; 1913.

¹² Coblentz, *Bur. Standards Scientific Papers Nos.* 45, 91, 97, 105, 131, 152, 156, 191.

¹³ Thwing, *Phys. Rev. (1)*, **26**, pp. 190–192; 1908.

¹⁴ Burgess, *Bur. Standards Scientific Paper No.* 121, 9 pp.

¹⁵ Randolph and Overholser, *Phys. Rev. (2)*, **2**, pp. 144–152; 1913.

¹⁶ Langmuir, *Amer. Electrochem. Soc. Trans.*, **22**, pp. 299–332; 1913.

¹⁷ Burgess, *Bur. Standards Scientific Papers Nos.* 62, 106; also Burgess and Waltenberg, 205.

tically no difference of temperature existing between the sample and the strip. The melting is almost instantaneous; the minute specimen either rolls up into a ball or spreads out into a thin film, depending upon the material and heating strip used.

In the present work the substances used were NaCl (800°C), Na_2SO_4 (884°), and Au (1063°). The samples were placed on the electrically heated nickel strip C, Fig. 1, previously heated until

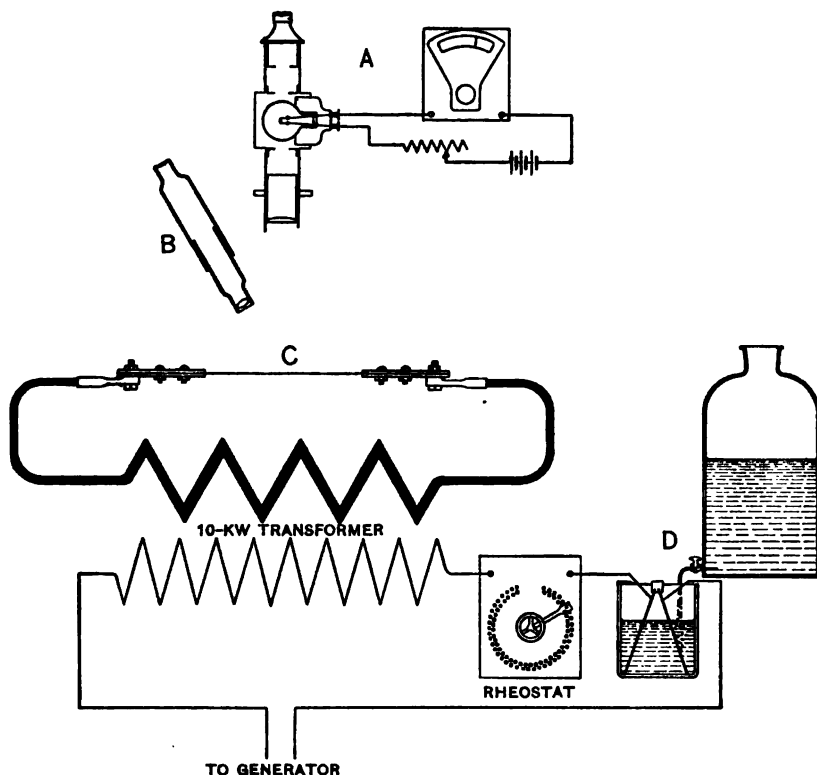


FIG. 1.—Method of microscopic melts

a firm coat of NiO had been formed, and the temperature gradually increased by means of the water rheostat D. The melting was observed by the microscope B, and the apparent temperature of the strip at the instant the melting occurred was measured by the optical pyrometer A. This instrument, a Holborn-Kurlbaum type of the Morse pyrometer, was carefully calibrated by two inde-

pendent methods—one, described by Waidner and Burgess,¹⁸ in which a compensated electrically heated porcelain black body of the Lummer-Kurlbaum type is used; and the other,¹⁹ in which a graphite black body is immersed in pots of molten metal. The calibrations by these two independent methods agreed to 1° C. The relation between the true temperature of the strip, the observed or apparent temperature, and the emissivity is expressed by:

$$\frac{I}{T} - \frac{I}{S_1} = \frac{\lambda}{0.4343 c_2} \log A_1$$

where T is the true absolute temperature, S_1 the observed absolute black body temperature for a wave length λ , c_2 the Planck or Wien constant and A_1 the absorption coefficient for a wave length λ . The emissivity is usually defined as the ratio of the intensity of light emitted by a nonblack material to that emitted by a black body at the same temperature. Hence A_1 = emissivity = absorptivity = $(1 - R_1)$ where R_1 is the reflection coefficient. The most recent determinations of the constant c_2 have been made by Coblenz,²⁰ who obtained as a final value $c_2 = 14\,465$ micron degrees, while the latest determinations at the Reichsanstalt range from 14 374 by Warburg²¹ and associates to 14 400 by Hoffmann and Meisner.²² A rounded value of 14 450 has been used in the present work. The following table presents a summary of results by this method:

TABLE 1
Emissivity of NiO by Microscopic Melts

$[\lambda = 0.65\mu]$

Observations	Material	True temperature	Observed temperature	Emissivity
		°C	°C	
6	NaCl	800	798	0.96 ₂
5	Na ₂ SO ₄	884	880	.93 ₂
8	Au	1063	1055	.90 ₂

¹⁸ Waidner and Burgess, Bur. Standards Scientific Paper No. 55, p. 165.

¹⁹ Kanolt, Bur. Standards Technologic Paper No. 10, p. 8; Foote, Metallurgical and Chem. Engin. 11, pp. 97-98; 1913.

²⁰ Coblenz, Bur. Standards Scientific Paper No. 204, p. 76.

²¹ Warburg, Leithäuser, Hupka, Müller; Preuss. Akad. Wiss., Berlin, Ber., 1, p. 35; 1913.

²² Hoffmann and Meisner, Ze. Instrk., 33, pp. 157; 1913.

SPECTROPHOTOMETRIC METHOD.—Some preliminary data were obtained by comparing the intensity of the radiation from the outside of a nickel tube electrically heated in air with that emitted from a small opening of a diaphragmed inclosure in the center of the tube. By properly locating suitable diaphragms throughout the interior of the tube black body conditions could be obtained quite satisfactorily. It was found more convenient, however, to employ the wedge method of Mendenhall,²³ the spectrophotometer replacing the optical pyrometers ordinarily used.

The use of spectrophotometer has among others one especial advantage in that slight fluctuations of the heating current affect both the inside and outside surfaces of the wedge alike and hence do not disturb the intensity relation of the two fields. When one pyrometer is used, taking readings alternately inside and out, these fluctuations become serious, especially if the emissivity is high and the difference between the apparent and true temperature of the wedge accordingly small. Two pyrometers, one sighted outside and one inside, and read simultaneously by different observers, only complicate matters on account of the errors of calibration of the instruments and the difference in settings likely to occur with two observers. Moreover, the computation of the emissivity from most pyrometric observations involves a knowledge of λ , the "center of gravity" of the red absorption screen. As has been shown by Waidner and Burgess²³ and by Pirani²⁴ this mean wave length depends upon the character and temperature of the radiating source sighted upon, and upon the visibility curve of the individual observer. It is not a true monochromatic transmission, or a narrow band, but a band containing nearly all the spectrum. This difficulty does not occur with the Wanner pyrometer or the spectral pyrometers of Mendenhall and of Henning in which the absorption screen is replaced by a dispersing prism. But even with a spectral pyrometer it is probable that the measurement of the difference of two temperatures which are nearly identical gives rise to greater error than the direct determination photometrically of two light intensities which are quite different.

²³ Waidner and Burgess, see 18, *idem.*, p. 175.

²⁴ Pirani, *Deutsch. Phys. Gesell. Verh.*, 1913, pp. 826-838.

Fig. 2 illustrates the optical arrangement used with a spectrophotometer of the Lummer-Brodhun type. It was found necessary on account of stray light to replace the Lummer-Brodhun cube by a silver-strip cube. The field of view thus obtained is represented by P. The dispersion of the spectrophotometer prism was calibrated by the spectral lines of Na, He, and several Fraunhofer lines. The spectral width of the emergent cone of

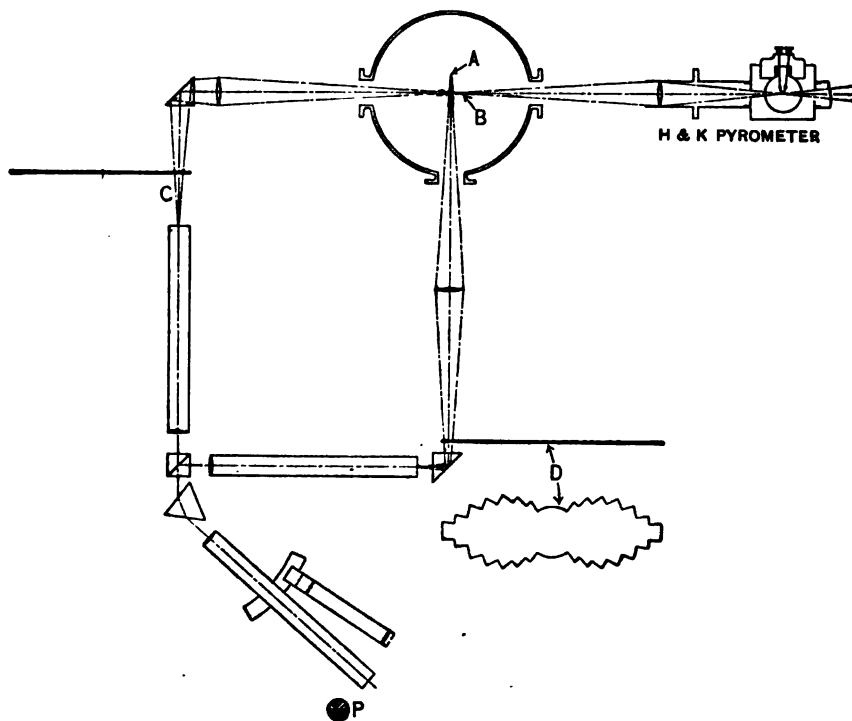


FIG. 2.—Spectrophotometer method

light was about $40\text{ m}\mu$ in the red and $20\text{ m}\mu$ in the violet. In making a series of observations the wedge was usually replaced by a source of light of approximately equal intensity in the direction AC and AD. The collimator slits were then adjusted until a match was obtained at P. The wedge was then inserted in the position A and a new match effected by adjusting the sector disks C and D without disturbing the collimator slits. Sector D was

used for preliminary adjustment when necessary. It consists of a 7-step disk with transmissions of 0.95, 0.90, 0.80, 0.70, 0.60, 0.50, and 0.40. The final adjustment was made with the disk C. This sector was designed by Brodhun²⁸ and is so constructed that any angular opening from 0 to 200° French system can be made while rotating at full speed, and by an arrangement of mirrors the scale in motion may be read to 0.01°. After a series of readings have been taken with the wedge in position A, the wedge is turned through 90° to position B and a new series made. A previous test

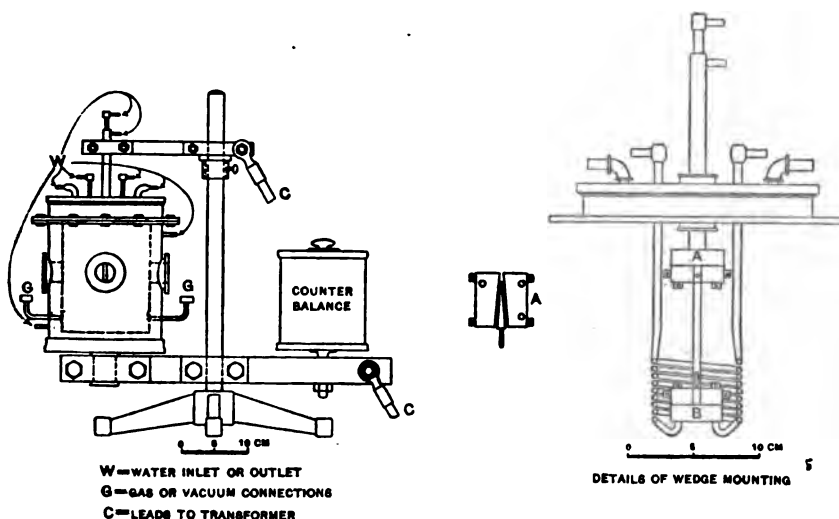


FIG. 3.—Method of mounting and heating wedge

has shown that both outer sides of the wedge emit with the same intensity. The zero adjustment of the spectrophotometer is thus obviated. The final intensity relation is obtained by taking the square root of the product of the intensity relations in positions A and B. Readings were taken in this manner for several temperatures, and color varying from $\lambda = 0.5\mu$ to 0.7μ .

Fig. 3 shows a sketch of the furnace used for holding and heating the wedge. The furnace was constructed a little more elaborately than necessary for this particular investigation for the reason that it will be employed subsequently for metals and oxides

²⁸ Brodhun, Zs. Instrk., 24, p. 313; 1904.

where it is desirable to use vacuum or an atmosphere of nitrogen or hydrogen. The entire furnace is water jacketed and so mounted that it may be conveniently rotated about its point of support in order to bring into the line of sight any one of the three windows illustrated in the figure. The wedge was mounted between a fixed water cooled contact A and a movable double spiral, water cooled, spring contact B. Such a mounting satisfactorily takes care of the expansion of the wedge on heating.

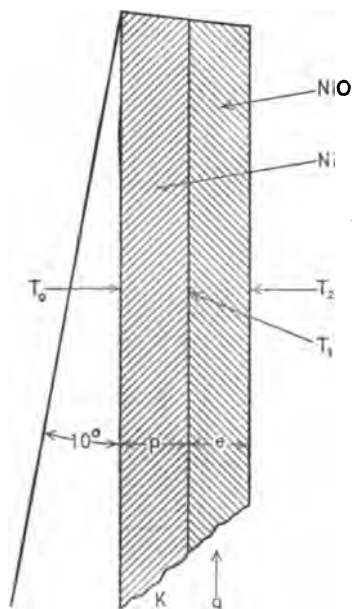


FIG. 4.—Magnified section of wedge

RADIATION FROM A WEDGE-SHAPED CAVITY.—Mendenhall,² following the method used by Féry²⁰ relative to the emission from conical cavities has shown that a wedge-shaped cavity of small angle emits practically black-body radiation. With a thin wedge there is practically no difference of temperature between the inside and outside surface. In the present work the wedge, heated in air, becomes coated with a thin layer of oxide which undoubtedly has a lower heat conductivity than the Ni. It is necessary to know what effect this thin homogeneous layer has on the temperature gradient through the wedge. The maximum gradient

effect can be obtained as follows. Assume that the oxide is non-conducting electrically and that the entire heat loss takes place on the outside of the wedge only. Fig. 4 represents a magnified section of the wedge:

T_0 = inside absolute temperature.

T_1 = absolute temperature at boundary of Ni and NiO.

T_2 = absolute temperature of outside surface.

p = thickness of Ni.

e = thickness of NiO.

²⁰ Féry, *Compt. rend.* 148, pp. 777-780; 1909.

- k = heat conductivity of Ni.
 q = heat conductivity of NiO.
 E = potential drop along 1 cm of strip.
 I = current density, i. e., current per cm^2 of cross section.
 b = total breadth of wedge, both outer sides.
 dT/dx = temperature gradient through Ni.
 R = specific resistance of Ni.
 Q = quantity of heat passing through oxide per cm^2 of surface per sec.

$$(1) \quad Q = q \frac{T_1 - T_2}{e} = I^2 R p = \text{amount of heat developed per second in section of Ni } 1 \times 1 \times p \text{ cm}^3.$$

$$(2) \quad T_1 - T_2 = I^2 R p e / q$$

Consider a thin lamina 1×1 cm in center of the nickel strip. Total energy per second developed in $1 \text{ cm}^3 = EI$ watts. Energy per second developed in a lamina $1 \times 1 \times x \text{ cm}^3 = xEI$ watts.

$$(3) \quad xEI = -kdT/dx$$

integrating between the limits $x = 0$ and $x = p$

$$(4) \quad EI p^2 / 2k = T_0 - T_1 = I^2 R p^2 / 2k$$

$$(5) \quad T_1 = T_0 - I^2 R p^2 / 2k$$

substituting in (2)

$$(6) \quad T_0 - T_2 = I^2 R p (p / 2k + e / q)$$

or

$$(7) \quad T_0 - T_2 = EI p (p / 2k + e / q)$$

The thickness of the Ni employed was about 0.010 to 0.015 cm. The oxide thickness varied from 0.002 cm after one hour heating at 1100°C to 0.005 cm after five hours. The heat conductivity, k , of nickel is known from Angell's²⁷ determinations, but no observations appear to exist for q . Even though q is assumed

²⁷ Angell, Phys. Rev. (1), **33**, pp. 421-432; 1911.

0.1 of k the second term in brackets in (7) is much greater than the first for a value of $e = 0.003$ or 0.005 cm. Since the variation of p with time of heating is small one may eliminate the e/q term by taking readings with successively thinner oxide layers and extrapolating the curve thus obtained to zero thickness or zero time of heating. When this is done T_2 becomes theoretically equal to T_1 ; hence:

For zero time $T_0 - T_2 = EI\rho^2/2k = \delta T$.

Let I'_2 refer to the intensity of light emitted by the NiO surface at a temperature T_2 .

I_0 refer to the intensity of light emitted by a black body at a temperature T_0 .

I_2 refer to the intensity of light emitted by a black body at a temperature T_2 .

The ratio of intensities measured by the spectrophotometer is:

$$(8) \quad \frac{I'_2}{I_0} = \frac{I'_2}{I_2 + \delta I}$$

The intensity ratio desired is:

$$(9) \quad I'_2/I_2$$

$$(10) \quad \text{By Wien's law: } I = c_1 \lambda^{-5} e^{-c_2/\lambda T}$$

$$(11) \quad \text{hence } \delta I = I \frac{c_2}{\lambda T^2} \delta T$$

substituting in (8), observed emissivity is as follows:

$$(12) \quad I'_2/I_0 = \frac{I'_2}{\left(1 + \frac{c_2}{\lambda T_2^2} \delta T\right) I_2}$$

$$(13) \quad \text{True emissivity} = \left(1 + \frac{c_2}{\lambda T_2^2} \delta T\right) \cdot (\text{observed emissivity}).$$

$$(14) \quad \text{Correction factor to observed data} = \left(1 + \frac{c_2}{\lambda T_2^2} \delta T\right)$$

Equation (14) represents therefore the correction which may be applied to observations on a film of oxide of negligible thickness.

The energy dissipated in the wedge is lost by end conduction, radiation, and convection. In the present work the air pressure inside the furnace was atmospheric, and hence the convection loss was high. Observations showed that the total energy loss from the wedge was from two to three times the loss by radiation. A part of the total energy loss must come directly from the wedge-shaped cavity. The small amount lost by radiation from the cavity may be computed, but it is difficult to determine the nature of the convection currents in this V-shaped opening. Equation (14) was derived on the assumption that all the energy was lost from the outside surface of the wedge. The radiation and convection losses from the interior of the wedge and the loss by conduction at the ends will lower the temperature gradient through the nickel as computed from the total power consumption, and hence lower the magnitude of the correction factor. The magnitude of the correction as derived above varies from 0.5 to 2 per cent for the experiments in question. On account of its being in reality very much smaller, and the exact correction not being conveniently determinable, no correction whatever has been applied to the data. It is probable that the uncorrected values are more accurate than the values increased by this maximum correction. Some slight advantage might have been gained in using a high vacuum, thus reducing the convection loss and the temperature gradient effect. Determinations in air at atmospheric pressure, however, are believed to be of sufficient accuracy and of greater interest.

METHOD OF OBSERVATION.—The nickel strip of dimensions about 6 by 9 by 0.014 cm was folded into a 10° wedge 3 by 9 cm, mounted in the furnace and electrically heated in air for several minutes until a smooth, tough coat of oxide formed. The current was so regulated that the temperature measured by the optical pyrometer remained constant throughout the series of observations. Spectrophotometric measurements were made at 10 to 12 wave lengths in the visible spectrum with the wedge first in position A and then in position B. The time of the observations was

recorded, counted from the initial flowing of the current. For each of a series of times varying from 0.2 to 6 hours, a spectral curve of emissivity was plotted. In all cases the relation E_λ vs. λ was practically linear. This operation was repeated independently for a number of different wedges. The emissivity observed at various times, for the three wave lengths $\lambda = 0.5, 0.6$, and 0.7μ

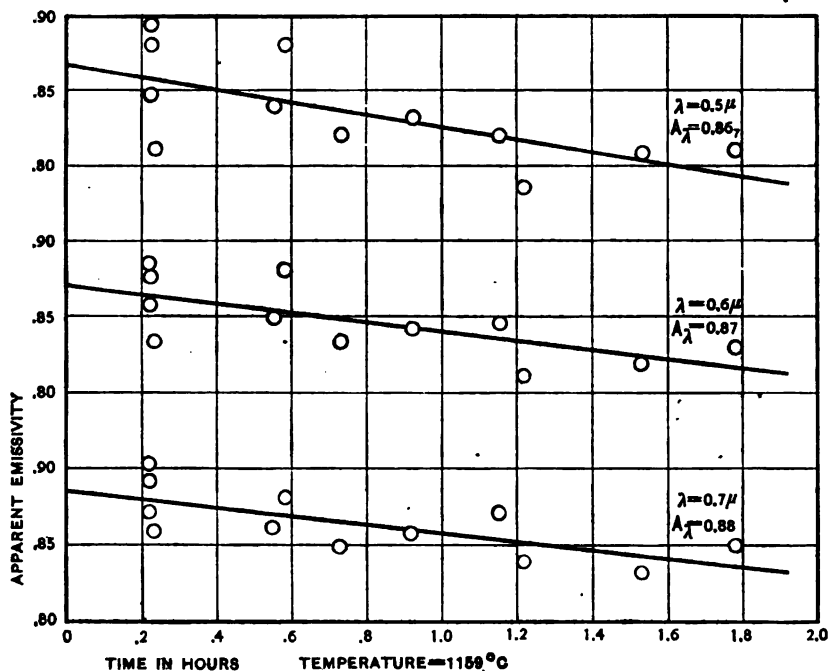


FIG. 5.—“Apparent” monochromatic emissivity as a function of the oxide thickness

(read from the spectral curves) was plotted, time vs. apparent or observed E_λ .

Fig. 5 represents a typical example of this procedure. Here are shown the independent determinations on 4 different wedges at an average temperature of 1159°C , for the above wave lengths. Each point is taken from a spectral curve observed at the indicated times. Within experimental error, a straight line may be drawn through the points. This line extrapolated to zero time represents the intensity relations for an extremely thin oxide layer, an ideal oxide layer which is thick enough to be opaque,

and hence one which possesses the same optical properties as a thick layer, but one so thin that the temperature gradient through it is practically nil. The extrapolated value of the intensity ratios is taken as the true emissivity of NiO. This process was repeated for 3 other temperatures, namely, 936, 1058, and 1255° C. A number of wedges were employed, each one being operated at a single temperature only. The reason for this is not that heating at, say, 1255° alters the character of the surface so that different values would be found on again lowering the temperature to 936°, but simply to avoid complicating the rate of formation of the oxide and thus altering the temperature gradient throughout the oxide layer. A number of observations were taken to justify the statement that the emissivity of the oxide does not depend upon its previous heat treatment, at least within the limits of the present experimental error.

CHARACTER OF THE OXIDE (analysis by J. R. Cain).—The nickel used contained a small amount of iron. One sample showed 0.8 per cent Fe. The oxide formed on heating in air is NiO with the above proportion of iron as FeO. When the black, tough coat of NiO was removed, a minute green film was detected, deposited on the nickel surface. This was so thin and in such small quantity that it was not possible to analyze it. It is very likely Ni_2O_3 , and is immediately converted into the black oxide NiO on heating in air. The existence of Ni_2O_3 , however, is questioned somewhat in Moissan's and Gmelin-Kraut's treatises, and its properties are not fully described.

RESULTS.—Fig. 6 presents the final observations on the dispersion of the emissivity of NiO in the range $\lambda = 0.5$ to 0.7μ for the temperatures 936, 1058, 1159, and 1255° C. Over this range of the spectrum the emissivity is found to increase with increasing wave lengths. The type of curves suggests the presence of an absorption band in the early infra red, but one which is probably broad and not well defined.

Fig. 7 illustrates the variation of emissivity with temperature for a wave length $\lambda = 0.65\mu$. The three points obtained by the method of microscopic melts lie well upon the curve determined by the spectrophotometric measurements. It has generally been

assumed that the emissivity in the visible spectrum of pure metals is independent of temperature. Mendenhall and Forsythe,⁷ however, have questioned this and have observed marked temperature coefficients of A_1 with several metals. For $\lambda = 0.658\mu$ they found that the emissivity of molybdenum, tantalum, and carbon decreases with increasing temperature, while for tungsten an increase of emissivity with increasing temperature takes place. It is well known that the emissivity of the rare earth oxides is dependent upon the temperature. There is accordingly no reason for expecting the monochromatic emissivity of NiO to be independent

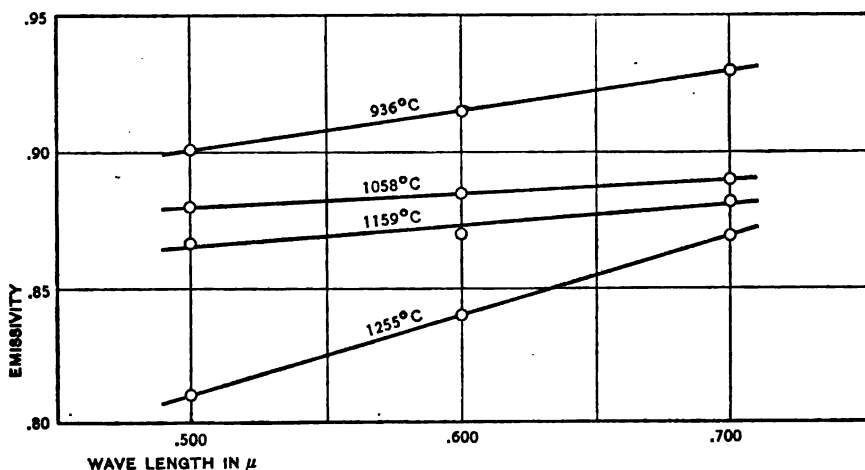


FIG. 6.—Monochromatic emissivity vs. wave length

of temperature. That the emissivity of NiO for any wave length in the visible spectrum decreases with increasing temperature is firmly established by the present observations.

In Fig. 8 are given the corrections in degrees centigrade which must be added to the temperature observed with an optical pyrometer using red light ($\lambda = 0.65\mu$), when sighted on NiO, in order to obtain the true temperature of the material. These corrections are small, amounting to only 20° at 1300°C .

In Table 3 are given the numerical values of these corrections to be applied to the observed temperatures, and the corresponding true temperatures, on both the Centigrade and Fahrenheit scales.

THE TOTAL EMISSIVITY OF NICKEL OXIDE

METHOD.—A strip of sheet nickel usually about 6 by 15 cm in size, mounted vertically, was electrically heated in air until a uniform, fairly thick coat of oxide was formed. Upon this strip were sighted normally radiation pyrometers of various types. The apparent temperatures for $\lambda=0.65\mu$ were obtained by means of an Holborn and Kurlbaum pyrometer and corrected to true temperatures according to the curve in Fig. 8. Observations were

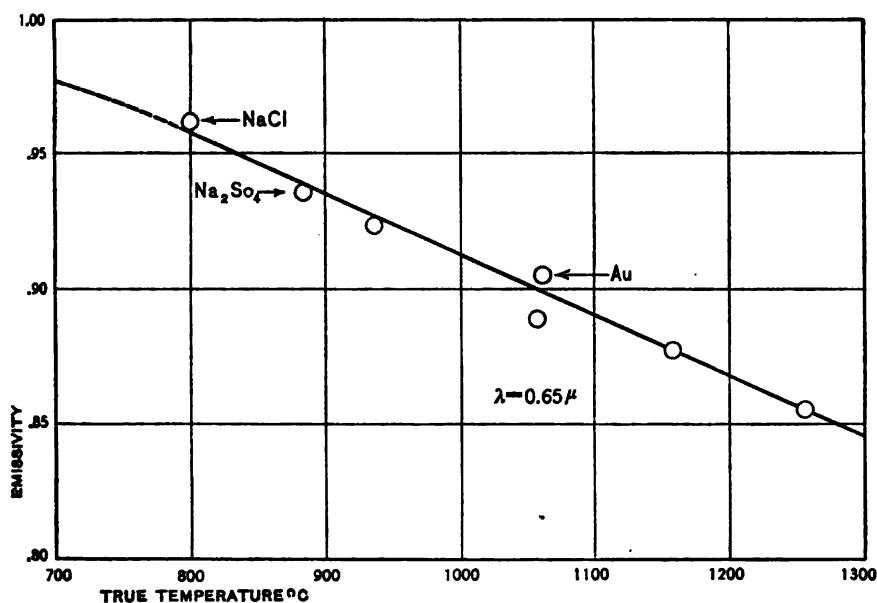


FIG. 7.—Monochromatic emissivity ($\lambda=0.65\mu$) vs. temperature

taken for a large number of different temperatures. The same strip could be used over the range 600 to 1200° and readings made at 600° both before and after heating to 1200° agreed in all cases. The previous heat treatment of the strip accordingly had no effect. In general each pyrometer was used for a series of readings on 4 or 5 different strips. Three sets of readings were taken with pyrometers sighted on a 2.5-cm nickel tube electrically heated. The results were the same as for the strips.

THE PYROMETERS.—Ten different pyrometers were employed. Three of these were of the Thwing²⁸ type and seven of the Féry²⁹ type. Two of the Thwing pyrometers were the ordinary long tube receivers with the thermoelement located at the apex of an aluminum reflecting cone. The other was the so-called permanent installation type in which the diaphragms are open to the air to prevent heating. In this instrument the open end of the cone was

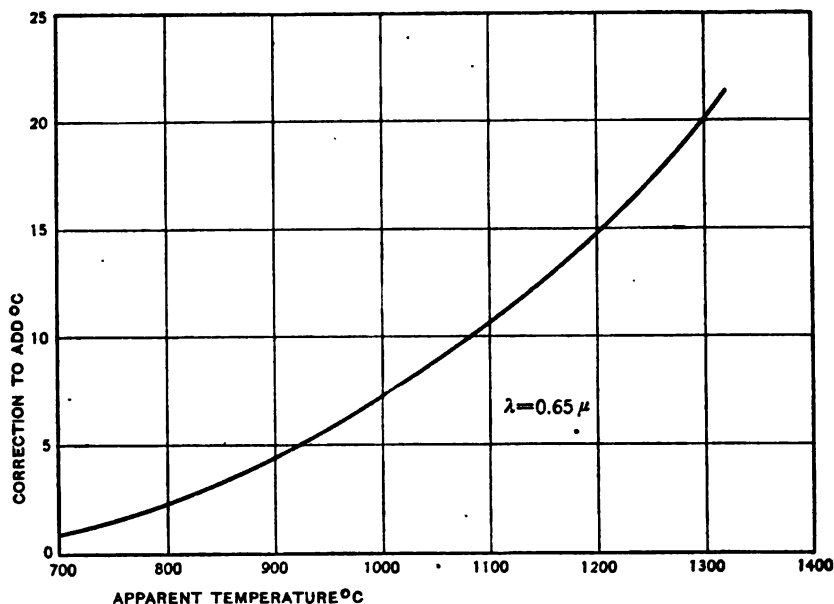


FIG. 8.—Corrections to optical pyrometer

covered by a thin mica window. Six of the Féry pyrometers were thermoelectric instruments with gold mirrors; the other was a Féry Spiral pyrometer, in which the thermoelement is replaced by a bimetallic spring which on expanding or contracting operates a movable pointer over a scale graduated in terms of temperature.

The relation between temperature and emf of the thermocouple type radiation pyrometers may be expressed by the empirical equation $e = a (T^b - T_0^b)$ where e is the emf developed by the

²⁸ Thwing, J. Frank. Inst., 165, pp. 363-370; 1908.

²⁹ Féry, Engineering, 84, pp. 539-540, 1907. Bull. d. Seances Soc. Franc. d. Physique, 1907, pp. 186-188.

thermocouple, the cold junction being at T°_{abs} and the hot junction a few degrees above this, depending upon T the absolute temperature of the black body upon which the pyrometer is sighted, and b is an empirical constant of approximate value 4.

The pyrometers³⁰ were calibrated by sighting into a (15 by 6 cm inside measurement) diaphragmed graphite black body mounted in a 60 by 8 cm platinum wound furnace, inclined 30° to the horizontal to mitigate air circulation. Kaolin diaphragms of proper aperture were located at various distances along the furnace to further prevent air circulation. The temperature of the black body was measured by two platinum-rhodium thermocouples which were calibrated in terms of the melting points of zinc, antimony, and copper. The readings of these couples were checked by an Holborn and Kurlbaum pyrometer sighted into the graphite black body. Exploration with a thermocouple through the 15-cm length of the black body showed a satisfactory temperature distribution (variations of less than 5° at 1300°). The readings of the optical pyrometer and of the thermocouples agreed to at least 5°, showing that black body conditions were sufficiently well obtained.

Two of the Féry instruments were used both with and without the diaphragm attachment, so that in reality 12 radiation instruments were employed.

The question of blackness of the receivers will be discussed in the paper mentioned above. It is sufficient to state here that only the selective absorption (i. e. variation of absorption or reflection coefficient with wave length) is of importance. The gold mirror³¹ of the Féry pyrometer reflects uniformly about 96%³² of the heat radiation from 1 to 14 μ . In the temperature range 600° to 1200° C only a small amount of the radiation can be affected by the selectivity of gold in the visible spectrum. The receivers are accordingly black or more accurately "gray," as far as the requirements of the present experiments are concerned.

³⁰ The subject of radiation pyrometry is one which has been briefly reported upon by the authors (Phys. Rev. (2), 3, pp. 77-8) and it is hoped to present the completed paper very shortly under the title "Some Characteristics of Radiation Pyrometers." For the reason that the various points which come up in the use and calibration of radiation pyrometers will there be treated in full, a complete discussion will not be given here.

³¹ Reflecting Power of Gold, Smithsonian Physical Tables.

³² Whipple, Engineering, 20, p. 1412; 1910.

THE APPLICATION OF RADIATION PYROMETERS TO THE DETERMINATION OF EMISSIVITY.—If E denotes the total emissivity of an approximately nonselectively radiating material at an absolute temperature T , and S the apparent absolute temperature of this material observed with an approximately nonselective receiver of the radiation pyrometer type, we have

$$(1) \quad E = \frac{S^4 - T_0^4}{T^4 - T_0^4}$$

Above 600° C the error involved in omitting the T_0 term is negligible. For example, if the emissivity is about 0.5, the error in E , arising from neglecting $T_0 = 300$, is about 0.007 at 600° C and 0.0002 at 1300° C. At higher values of E the error is still smaller. Hence it is possible to write:

$$(2) \quad E = S^4/T^4$$

Expressed in terms of emf where e denotes the emf developed by a thermoelectric radiation pyrometer sighted on a black body of temperature $T^{\circ}\text{abs}$ and e' the emf developed when sighted on a nonblack approximately nonselectively radiating substance of apparent temperature $S^{\circ}\text{abs}$ and true temperature T° , (2) becomes;

$$(3) \quad E = (e'/e)^{4/b}$$

where b is the characteristic exponent of the empirical equation $e = aT^b$.

Equation (3) was used in the computation of the emissivity determinations for all the pyrometers except the Féry Spiral, for which equation (2) was employed.

RESULTS.—Table 2 presents the data upon total emissivity for a series of temperatures from 600 to 1300° C. Each horizontal line represents the observations by any one instrument, the values being taken from a smooth curve of emissivity vs. true temperature of NiO for the indicated pyrometer. This curve was determined by from 20 to 60 independent observations at various temperatures and on several nickel strips. The averages of the determinations by the different pyrometers are given in line 13.

TABLE 2
Total Emissivity, Summary of Observations

Weight	Temperature °C											Expo- nent					
	600	650	700	750	800	850	900	950	1000	1050	1100		1150	1200	1250	1300	Pyrometer
1	0.74	0.75	0.76	0.76	0.77	0.78	0.79	0.80	0.81	0.84	0.89	0.94	0.97			Thwing 983 box receiver	4.32
2			.55	.59	.62	.64	.65	.66	.67	.71	.77	.85	.89	0.92	0.93	Thwing 984 tube receiver	3.56
2		.60	.63	.65	.67	.69	.70	.72	.74	.77	.81	.86	.90	.92	.92	Thwing 985 tube receiver	3.68
2			.74	.76	.78	.80	.82	.84	.85	.87	.89	.90	.90	.88		Fery thermoelectric 10509	3.96
2	.47	.55	.63	.70	.77	.80	.83	.84	.84	.85	.85	.84	.83	.81	.81	Fery thermoelectric 5967	3.87
2	.56	.63	.68	.73	.77	.79	.81	.82	.84	.84	.84	.84	.82	.81	.79	Fery thermoelectric 323	3.84
2		.60	.62	.64	.65	.67	.68	.69	.71	.72	.75	.79	.83	.85	.86	Fery thermoelectric 10537	3.53 to 4.55
2	.46	.49	.52	.55	.58	.61	.64	.67	.69	.72	.75	.78	.81	.84	.86	Fery thermoelectric B. S. 30	3.78
2	.51	.53	.55	.56	.58	.59	.61	.63	.66	.71	.77	.83	.86	.87	.88	Fery thermoelectric B. S. 30 with diaphragm	3.90
2	.51	.54	.57	.60	.62	.65	.68	.70	.73	.76	.79	.81	.84	.86	.88	Fery thermoelectric 10530	4.22
2	.59	.60	.61	.62	.64	.65	.66	.68	.70	.74	.79	.83	.85	.87	.88	Fery thermoelectric 10530 with diaphragm	4.26
1	.72	.74	.76	.79	.81	.83	.85	.87	.88	.89	.90	.91	.92	.92	.92	Fery spiral	
	.54	.59	.62	.65	.68	.70	.72	.73 ₅	.75	.78	.81	.84	.86	.865	.867	Mean	
	.02	.02	.02	.02	.02	.02	.02	.02	.02	.01	.01	.01	.008	.008	.01	Probable error of mean	

Below these are indicated the probable error of the mean. This ranges from $\pm .01$ to $\pm .02$. It can not be claimed, of course, that the actual total emissivity relations of NiO are determined with this accuracy on account of the possibility of some systematic error, but it would appear probable that the correct values are not far different from the above mean values obtained with 12 independent series of observations by pyrometers possessing marked differences in their characteristics as illustrated in the wide variation of the exponent b .

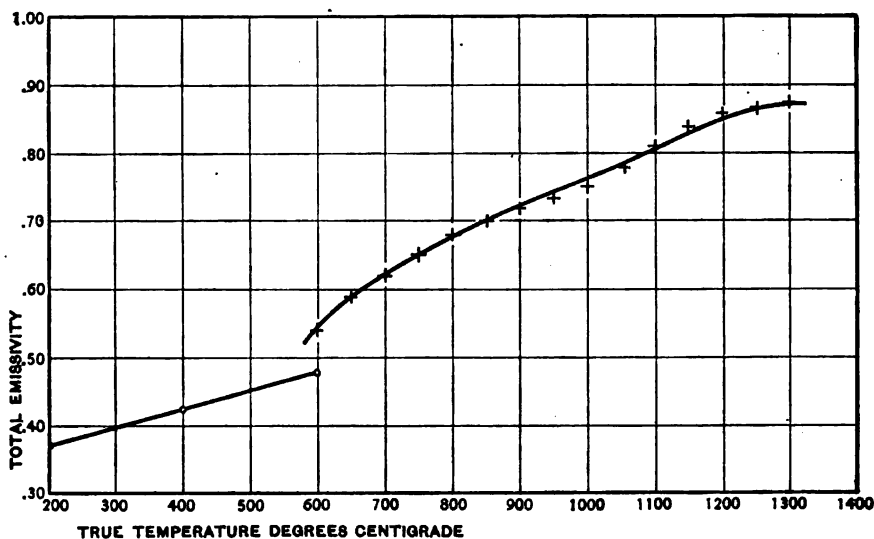


FIG. 9.—Total emissivity vs. temperature

In Fig. 9 are plotted the final observations which definitely establish the increase of the total emissivity of NiO with temperature. Randolph and Overholser, working in the range 200 to 600°, observed a similar increase. In the range 700 to 1200° the present work shows the increase is nearly linear with temperature. Obviously this linear relation will not extend indefinitely, for it can not exceed 1.00 or become zero. The characteristic curve must therefore be S shaped. This departure from the straight line is apparent at 1200 to 1300°. It is possible that the emissivity at still higher temperatures increases very slightly and gradually until the melting of the oxide may bring about a discontinuity in the curve.

Somewhere below 600° the curve must again change its slope, possibly becoming approximately parallel to the axis of temperatures.

TABLE 3
Optical Pyrometer ($\lambda=0.65\mu$) Sighted on Nickel Oxide

Observed temperature	Correction to add	True temperature	Observed temperature	Correction to add	True temperature
$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$
700	1	701	1200	1	1201
800	2	802	1400	3	1403
900	4	904	1600	6	1606
1000	7	1007	1800	12	1812
1100	10	1110	2000	18	2018
1200	15	1215	2200	27	2227
1300	20	1320	2400	39	2439

The three points represented in Fig. 9 by circles are from the data of Randolph and Overholser. It is possible to extend our curve so that it will coincide with the 400 and 200° points determined by these investigators. The disagreement of the two curves at 600 , however, would indicate a systematic difference between the two sets of data.

TABLE 4
Total Radiation Pyrometer Sighted on Nickel Oxide

Observed temperature	Correction to add	True temperature	Observed temperature	Correction to add	True temperature
$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$	$^{\circ}\text{F}$
500	120	620	900	220	1120
550	115	665	1000	205	1205
600	110	710	1100	195	1295
650	105	755	1200	185	1385
700	100	800	1300	180	1480
750	95	845	1400	170	1570
800	95	895	1500	165	1665
850	90	940	1600	155	1755
900	85	985	1700	150	1850
950	80	1030	1800	135	1935
1000	75	1075	1900	125	2025
1050	70	1120	2000	115	2115
1100	65	1165	2100	105	2205
1150	60	1210	2200	95	2295
1200	55	1255	2300	95	2395
1250	50	1300			

Fig. 10 represents the corrections in degrees centigrade which must be added to the temperature observed with a total radiation pyrometer sighted on NiO in order to obtain true temperatures. On account of the rapid increase of the emissivity with temperature these corrections decrease up to the apparent temperature 1250°. Above this range they probably increase, since here the rate of increase of emissivity with temperature is small.

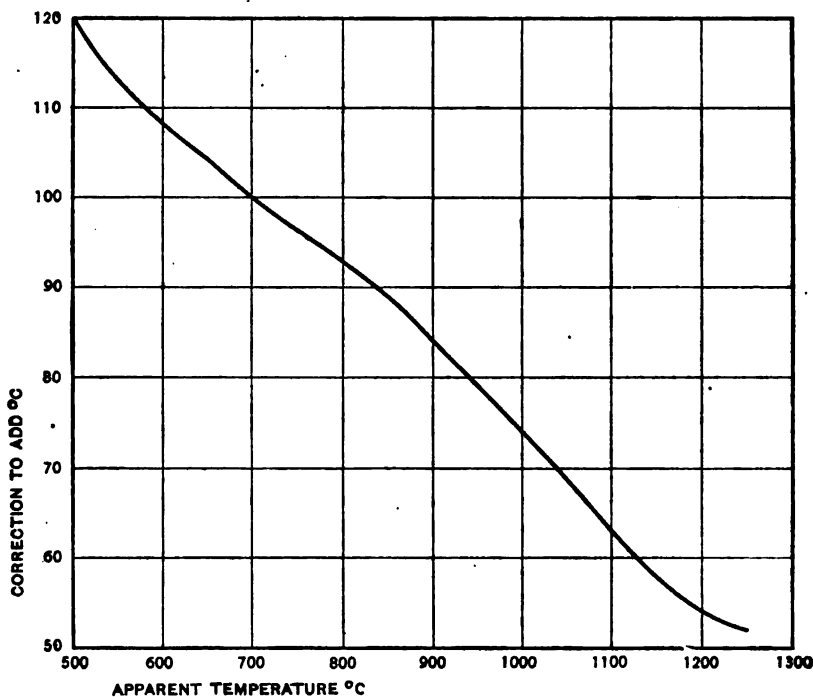


FIG. 10.—Corrections to total radiation pyrometer

In Fig. 11 are plotted the number of watts per cm² radiated by NiO at various temperatures. For comparison, a similar curve for a black body is given computed from the equation $J = \sigma(T^4 - T_0^4)$ where $\sigma = 5.7 \times 10^{-12}$ watts cm⁻² deg⁻⁴ and $T_0 = 300^\circ$.

Table 4 shows the numerical values of the corrections to be applied to the observed temperatures, both Fahrenheit and centigrade scale, and the corresponding true temperatures for use with any type of total radiation pyrometer.

SUMMARY.—The monochromatic emissivity or absorptivity of nickel oxide (NiO) has been measured for the temperature interval 700 to 1300°C, and its dispersion has been observed spectrophotometrically from $\lambda = 0.5$ to 0.7μ for four temperatures in this range.

The monochromatic emissivity increases linearly with increasing wave length throughout the visible spectrum and decreases linearly with temperature from 700 to 1300°C.

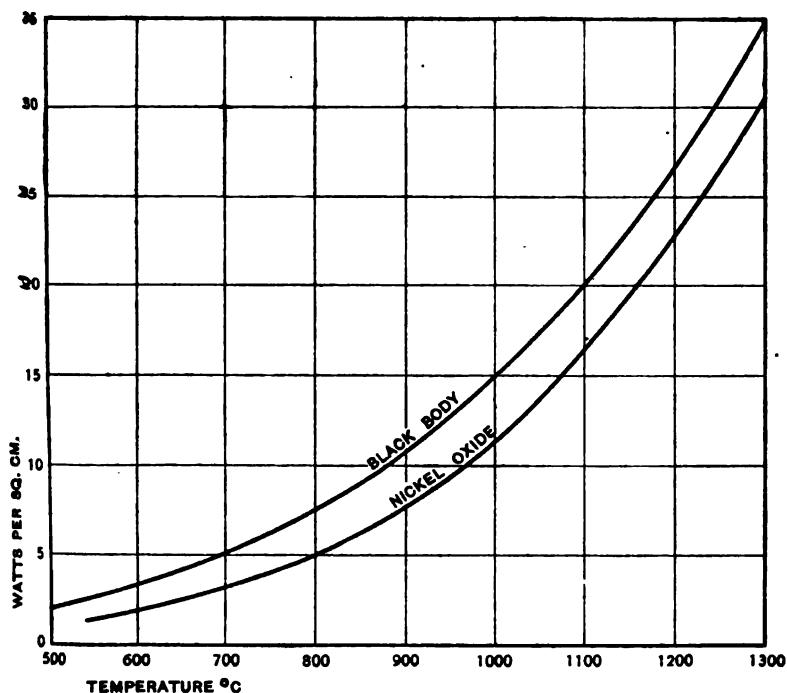


FIG. 11.—Radiation loss from NiO and from a black body

Determinations of the emissivity for $\lambda = 0.65\mu$ with an optical pyrometer by the method of microscopic melts agreed with the spectrophotometric determinations by the Mendenhall wedge method.

The total radiation of nickel oxide has been studied by use of 12 receivers sufficiently "black" for the requirements of this experiment.

The total emissivity increases with temperature in the interval 600 to 1300° C.

Correction curves and tables are given for use with optical pyrometers of the Wanner, Scimatco, Morse, Le Chatelier, Féry Absorption, Shore, and Holborn-Kurlbaum type instruments using red light ($\lambda = 0.65\mu$), and for radiation pyrometers of the Féry, Foster, and Thwing types.

In conclusion, the writers desire to thank the Taylor Instrument Cos. of Rochester, the Thwing Instrument Co., and the Brown Instrument Co. of Philadelphia for very generously placing at their disposal several radiation pyrometers. Mention is due Messrs. Kellberg and Sale for assistance in some of the observations.

WASHINGTON, April 15, 1914.



ADJUSTMENTS OF THE THOMSON BRIDGE IN THE MEASUREMENT OF VERY LOW RESISTANCES

By F. Wenner and E. Weibel

In a previous paper¹ the desirability of making certain adjustments in addition to those necessary for establishing the principal balance of the Thomson bridge is discussed and the procedure followed in the Bureau of Standards for making these adjustments is given. The purpose of this paper is to describe somewhat different procedures which have been found to be better in case the resistances under comparison are extremely low.

Referring to Fig. 1, X and Y represent the low resistances under comparison, A and B represent those parts of the resistances of the main ratio arms between n and g , and between g and o ; α and β represent those parts of the resistances of the auxiliary ratio arms between n' and g' ; and between g' and o' ; and C represents the resistance between X and Y (approximately the difference in potential between n' and o' divided by the test current). The resistances of the connections between the low resistances (including that of their leads to the potential terminals) and the terminals n , n' , o , and o' of the double ratio set are represented by x_1 , x_2 , y_1 , and y_2 . The branch points to the galvanometer are represented by g and g' and to the battery or other source of current by b and b' .

In the previous paper it was shown that the equation for the Thomson bridge could be put in the following form:

$$X = Y A/B [1 + a + D (a - b)] \quad (1)$$

where a and $D (a - b)$ are small correction terms. More specifically a is the difference (in proportional parts) between the value of the

¹ Wenner, this Bulletin, 8, p. 580; Reprint No. 181; 1912.

main ratio, $(A + x_1)/(B + y_1)$, and A/B ; $a - b$ is the difference (in proportional parts) between the value of the main and auxiliary ratios, and D is approximately equal to the ratio of C to $X + Y$. The purpose of the auxiliary adjustments is to make these correction terms negligibly small and thus save the time which otherwise would be required for determining their magnitudes.

If a switch or other means is provided for opening the low resistance connection between X and Y , the bridge can readily be changed from a double (Thomson) to a simple (Wheatstone) bridge and back to a double bridge by simply opening and closing the switch. If, in addition, a means is provided for changing the

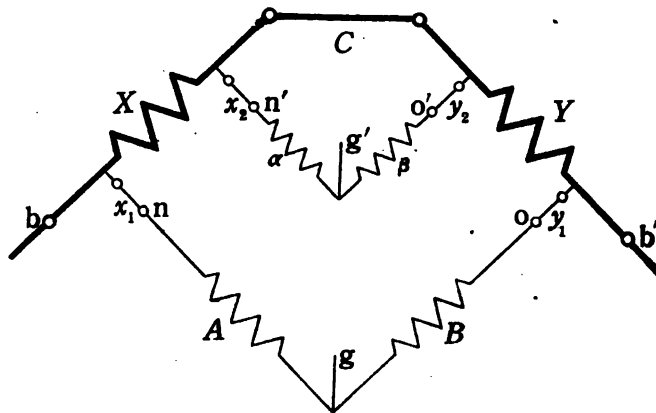


FIG. 1

resistances of the auxiliary ratio without changing those of the main ratio, $a - b$ can be made very small, so that if D is considerably less than unity the correction term $D(a - b)$ can be made negligible. This procedure, first published by Reeves,² is now used in most of the precise measurements of low resistances by the Thomson bridge method.

To keep D less than unity—that is, C less than $X + Y$ —is difficult if X and Y are both small—0.00001 ohm or less. In such cases the use of a switch is more or less impracticable, on account of its resistance and to open and close the connection at a terminal of one of the resistances one or more times during each measurement requires a considerable amount of extra work. Also the

² Proc. Phys. Soc. London, 14, p. 166; 1896.

time required, in some cases, makes it impossible to follow changes in the resistances caused by rapid changes in their temperature. It therefore seemed advisable to see if a method could be devised for making the adjustments without the repeated opening and closing of the low resistance connection between X and Y . On investigation two satisfactory procedures were found. Both require the use of a variable double ratio-set so adjusted that for any setting of the dial-switches the lack of equality of the two ratios A/B and α/β is so small that no appreciable error is introduced on this account. The first also requires the use of two

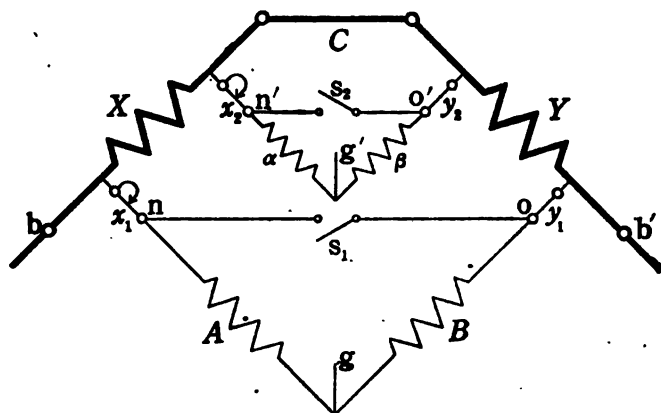


FIG. 2

switches s_1 and s_2 (see Fig. 2), and of adjustable low resistances¹ in the connectors x_1 and x_2 .

The procedure for the first method then is as follows:

1. With the connections as shown in Fig. 2, s_1 and s_2 open, the bridge is balanced by an adjustment of the dial switches of the double ratio-set.
2. With the switch s_1 closed² the bridge is balanced by an adjustment of the variable low resistance forming a part of x_1 .
3. With the switch s_1 open and s_2 closed, the bridge is balanced by an adjustment of the variable low resistance forming part of x_2 .
4. With the switches s_1 and s_2 both open, the bridge is balanced by an adjustment of the dial switches of the double ratio-set.

¹ Jaeger and Diesselhorst: Wiss. Abhandl. d. P.-T. Reichsanstalt, 4, p. 119; 1904.

The first adjustment makes A/B , approximately, equal to X/Y ; the second makes the correction term a negligibly small, the third makes b very small, and therefore the correction term D ($a-b$) negligibly small, and the fourth makes

$$\frac{A}{B} = \frac{X}{Y}. \quad (2)$$

If the fourth adjustment requires much change in the reading of the dial switches, the second and third adjustments may be disturbed slightly. In that case the second, third, and fourth adjustments should be repeated, and only the last reading of the dial switches used.

The second procedure requires that, instead of the switches s_1 and s_2 , means be provided for connecting a battery to the terminals n and o and to n' and o' . The procedure then is as follows:

1. With the test current supplied through the terminals b and b' , the bridge is balanced by an adjustment of the dial switches of the double ratio-set.

2. With the test current supplied through the terminals n and o , the bridge is balanced by an adjustment of the variable low resistance forming a part of x_1 .

3. With the test current supplied through the terminals n' and o' , the bridge is balanced by an adjustment of the variable low resistance forming a part of x_2 .

4. With the test current supplied through the terminals b and b' , the bridge is balanced by an adjustment of the dial switches of the double ratio-set.

Each of these adjustments accomplishes the same purpose as the corresponding adjustment of the first procedure.

Both procedures accomplish the desired result about equally well.

WASHINGTON, May 25, 1914.

QUANTITATIVE EXPERIMENTS IN RADIOTELEGRAPHIC TRANSMISSION

By L. W. Austin

The testing of the recently erected high-power United States naval radiotelegraphic station at Arlington, Va., has given another opportunity for carrying out experiments on the relation between the currents in sending and receiving antennas at various distances, and at the same time for investigating the relative advantages of transmission by means of damped and continuous oscillations.

The work of the Navy Department on quantitative long-distance transmission was begun in 1909, and during the autumn of that year and in 1910 experiments were carried on between the Brant Rock Station and the scout cruisers *Birmingham* and *Salem*. An account of this work was published in the Bulletin of the Bureau of Standards.¹

The results of the experiments were expressed by the empirical formula²

$$(1) \quad I_R = 4.25 \frac{h_1 h_2 I_s}{\lambda d} \cdot e^{-\frac{0.0015d}{\sqrt{\lambda}}}$$

where I_R is the received antenna current through a resistance of 25 ohms, I_s the sending current, h_1 and h_2 the full heights of the sending and receiving flat top antennas respectively, λ the wave length, and d the distance between the stations, the currents being given in amperes and the lengths in kilometers. The expression is applicable only to day³ communication over salt water. This formula was not expected to give highly accurate

¹ This Bulletin, 7, p. 315, 1911, Scientific Paper 159; Jahrbuch der drahtlosen Telegraphie, 5, p. 75, 1912.

² In formula (1) h denotes the total height of the flat-top antenna as in the former article. In all other cases in this paper h is the effective height of the antenna; that is, one-half the length of the equivalent Hertzian oscillator.

³ Day signals are, in general, fairly uniform in their intensity. Night signals are usually stronger but are so irregular in intensity that it has not been found possible to represent them by any quantitative expression

results, since the receiving resistance was taken arbitrarily as 25 ohms, which is too high for the shorter wave lengths and too low for the longer ones. It has, however, amply proved its usefulness as a practical expression for determining the range of communication between stations, and indicates with a fairly close degree of approximation the strength of signals which may be expected at any distance, at least up to 2000 miles (3700 km).

In 1909, Sommerfeld⁴ gave a theoretical treatment of the transmission of electrical waves over a plane perfectly conducting surface placed in the equatorial plane of a Hertzian oscillator. This theoretical work has been carried further by H. Poincaré,⁵ J. W. Nicholson,⁶ H. March,⁷ and W. von Rybczynski.⁸ Without discussing this work in detail the results may be stated in the following formula for the electric amplitude E .

$$(2) \quad E = 120\pi \frac{hI_s}{\lambda d} \sqrt{\frac{\theta}{\sin \theta}} \cdot e^{-\frac{0.0019d}{\sqrt{\lambda}}}$$

This formula may be analyzed into three parts. The first, $120\pi \frac{hI_s}{\lambda d}$, where h represents the effective height⁹ to the center of capacity of the sending antenna, λ the wave length, I_s the current at the base of the sending antenna, and d the distance to the point under consideration, is simply the Hertzian expression for the electric field produced at a distance d in the equatorial plane of an equivalent oscillator of length $2h$. It is supposed in this expression that the distance d amounts to a large number of wave lengths. The expression $\sqrt{\frac{\theta}{\sin \theta}}$ takes account of the curvature of the earth, θ representing the angle under which the distance d appears from the center of the earth. For purposes of calculation the expression may be considered equal to unity for all distances as yet covered by day transmission.

⁴ A. Sommerfeld, *Ann. der Phys.*, **28**, p. 665; 1909.

⁵ H. Poincaré, *Jahrb. d drahtl. Teleg.*, **3**, p. 445; 1910.

⁶ J. W. Nicholson, *Phil. Mag.*, **21**, p. 287. 1911.

⁷ H. March, *Ann. d Phys.*, **37**, p. 29; 1912.

⁸ W. von Rybczynski, *Ann. d Phys.*, **41**, p. 191; 1913. See also J. Zenneck, *Lehrbuch der drahtlosen Telegraphie*, p. 294.

⁹ If the earth is perfectly conducting and there are no metal masses near the antenna affecting the field distribution, h should equal the height to the center of capacity, and is so used except when special experiments showed the effective height to be less.

The final expression, the scattering term, $e^{-\frac{0.0019d}{\sqrt{\lambda}}}$ gives the losses due to the escape of energy into the upper atmosphere on account of the failure of the waves to follow perfectly the curvature of the earth. In this theoretical formula (2) the electric field will be expressed in volts per kilometer if I_s is expressed in amperes and all the lengths in kilometers. The equation is developed on the assumption of a perfectly conducting earth. According to von Rybczynski¹⁰ a slight departure from perfect conductivity will produce a slight increase in the receiving field strength, apparently on account of a diminution in the value of the scattering factor. If the conductivity of the surface becomes still poorer, however, an absorption term¹¹ would have to be introduced, as it is well known that the electrical waves are considerably absorbed in passing over land in most localities.

If the waves under consideration are undamped, the current in the receiving antenna is

$$(3) \quad I_R = \frac{Eh_2}{R} = 377 \frac{h_1 h_2 I_s}{\lambda d R} e^{-\frac{0.0019d}{\sqrt{\lambda}}}$$

h_2 represents the effective height to the center of capacity of the receiving antenna, expressed in kilometers, and R the high frequency resistance of the receiving system. In the case of damped oscillations, on account of the form of the wave train of oncoming oscillations, the value of the received current

$$(4) \quad I_R = \frac{Eh_2}{R \sqrt{1 + \frac{\delta_1}{\delta_2}}} = 377 \frac{h_1 h_2 I_s}{\lambda d R \sqrt{1 + \frac{\delta_1}{\delta_2}}} e^{-\frac{0.0019d}{\sqrt{\lambda}}}$$

where δ_1 and δ_2 are the decrements of the sending and receiving systems.

It is of course of the greatest importance to determine whether the actual observations on received current agree with the theoretical formula, both regarding the Hertzian term and the scattering term. The Brant Rock experiments did not conclusively settle these questions, especially the latter, as the greatest distance in the experiments, 1000 miles (1850 km) was too short, considering the errors of observation. Von Rybczynski in his

¹⁰ Ann. d Phys., 41, p. 208; 1913.

¹¹ See J. Zenneck, Ann. d Phys., 23, p. 846, 1907; A. Sommerfeld, Ann. d Phys., 28, p. 665, 1909; J. Zenneck, Lehrb. d drahtl. Telegr., p. 297.

article gives a curve in which the Brant Rock observed values are shown to agree more perfectly with the theoretical formula than with the empirical formula. Unfortunately, however, the observations chosen by him were among the earliest and least accurate in the series of experiments.

The high-power station at Arlington, Va., was equipped by the National Electric Signaling Co. with a 100-kw rotary gap sending set, and was intended for communication with the Canal Zone and with the fleet in the North Atlantic Ocean. The original plan for the antenna as submitted by the National Electric Signaling Co. showed an umbrella supported by a single tower 600 feet (182 m) high. The experiments at Brant Rock, however, showed the experts of the Navy Department that an umbrella antenna gave a center of capacity too low for the most effective working unless a very high mast and a large tract of ground were used. For this reason the Arlington station has been supplied with a platform antenna supported by three towers about 120 m between centers, one being 600 feet (182 m) high and the other two 450 feet (137 m). The antenna has been put up in sections and consists of two flat top antennas 350 feet (106 m) long and one 313 feet (96 m) long. These are 88 feet (26.8 m) wide with 23 wires each. The triangular space between the flat tops was filled in with a triangular fan.¹² of 25 wires supported independently of the flat top sections. The vertical portion of the antenna consisted of a fan of 23 wires, narrowing down to a point at 23 m above the earth, from which the wires are brought down in a cage of the Fessenden type. The capacity of this antenna is 0.010 μ f, its natural wave length approximately 2100 m, and its height to the center of capacity 122 m. The ground system consists of a radiating net work of wires covering the space between the triangle of towers and extending to some distance outside. The towers were built so that they were insulated from the earth with switches by which they could be connected to the ground net system. With the towers insulated, the antenna resistance, exclusive of the inductance, at a wave length of 4000 m is approximately 8 ohms. Grounding the towers reduces the resistance to

¹² At the close of the Salem experiments this fan was removed, as its swaying at times rendered the tuning slightly uncertain.

1.8 ohms, and curiously enough no perceptible difference in capacity is observed, nor is the natural period changed by more than a few meters. Theoretically it is difficult to understand how this great difference in antenna resistance can be produced without changing the field distribution so as to vary the capacity and wave length; but more remarkable still it is found that the ratio between the current in a receiving antenna a few miles distant and the sending current at Arlington remains unchanged whether the towers are grounded or insulated. Since the sending current with the towers grounded is much larger than with the towers insulated, they are always kept grounded. The receiving at Arlington is practically the same whether the towers are grounded or ungrounded. The decrement of the emitted waves at 3800 m is approximately 0.05.

SHORT-RANGE EXPERIMENTS

Short-range experiments have been made between several receiving stations near Washington, using the high-power station at Arlington and the station at the Washington Navy Yard for sending. For calculating the received current at these distances only the first part of the theoretical formula (4) need be used. The received current should then be

$$(4') \quad I_R = 377 \frac{h_1 h_2 I_s}{\lambda d R \sqrt{1 + \frac{\delta_1}{\delta_2}}}$$

In this case the lengths may be taken in any corresponding units since they occur an equal number of times in numerator and denominator. The receiving current was measured by thermoelements or thermomilliammeters.

Table 1 gives the results of these observations. The column of calculated values contains those derived from equation (4'), where the length of the equivalent oscillator is assumed to be twice the height¹³ to the center of capacity. All these observations indicate that the length of the equivalent oscillator is in

¹³ Ze-neck, *Lehrbuch d. drahtlose Telegraphie*, p. 46. In some earlier publications, *J. Washn Acad.*, 1, p. 275, 1911, and *Proc. Amer. Phil. Soc.*, 52, 210, p. 407, 1913, I have assumed the length of the equivalent oscillator to be $h\sqrt{2}$ instead of $2h$. (See R. Ruedenberg, *Ann. der Phys.*, 25, p. 446, 1908.) I have become convinced, however, that for the theoretical calculation of the electric field produced by the radiation, the equivalent length of the oscillator should be $l=2h$.

these cases not greater than the height to the center of capacity of the sending antenna, and in some cases is less.¹⁴ This may be due to the shape of the antennas, or, to the fact that the earth is not properly conducting as assumed in the theory. At Arlington there is undoubtedly some loss in the steel towers. The Washington Navy Yard station has its antenna supported by a wooden mast and a brick chimney in which there can be no losses; the ground, however, is not ideal.

TABLE 1
Short-Range Experiments

Sending station	Receiving station	λ meters	I_s amp.	Distance		h_1 meters	h_2 meters	R ohms	Received current 10^{-4} amp.		Obs. Cal.
				Miles	Km				Obs.	Cal.	
Arlington...	Bureau of Standards.	3800	102	4.2	7.8	122	30	275	5.8	15.8	0.37
Do.....	Capitol.....	3800	102	3.45	6.4	122	36	294	8.5	21.5	.40
Do.....	Navy yard.....	3800	102	3.9	7.2	122	36	282	9.3	19.9	.47
Navy yard...	Bureau of Standards.	1000	12.2	5.4	10.0	36	30	71	3.2	7.3	.44
Do.....	Capitol.....	1000	12.2	1.05	1.9	36	36	181	7.4	18.5	.40
Do.....	Bureau of Standards.	2800	7.0	5.4	10.0	36	30	70	0.55	1.07	.51
Do.....	Arlington.....	2800	7.0	3.9	7.2	36	122	9.3	22.0	46.2	.48

LONG-DISTANCE OBSERVATIONS

During the months of February and March, 1913, the cruiser Salem was sent on a voyage to Gibraltar for the purpose of carrying out tests with the Arlington station. Shunted telephone observations were taken in the day time up to 1920 nautical miles (3550 km), while with the Fessenden heterodyne messages were read by day up to 2100 nautical miles (3880 km). The wave length used by Arlington was 3800 meters and the average sending current was 100 amperes.¹⁵

The height of the Arlington antenna to the center of the horizontal portion is 470 feet (143 m) and the height to the center of capacity 400 feet (122 m). The height to the flat top of the Salem's antenna was 130 feet (39.6 m), the height to the center of capacity being 114 feet (34.5 m).

¹⁴ According to the results of M. Reich (*Physik. Zs.*, 4, p. 934, 1913), under favorable circumstances the theoretical value is more nearly approached than in my observations.

¹⁵ The original ammeter reading in the antenna was 110 amperes, but a later calibration of the instrument showed that this was somewhat too large.

The results of the observations with the electrolytic detector are shown in Fig. 1. The observed values of the received currents are indicated by crosses, and were calculated from the audibility

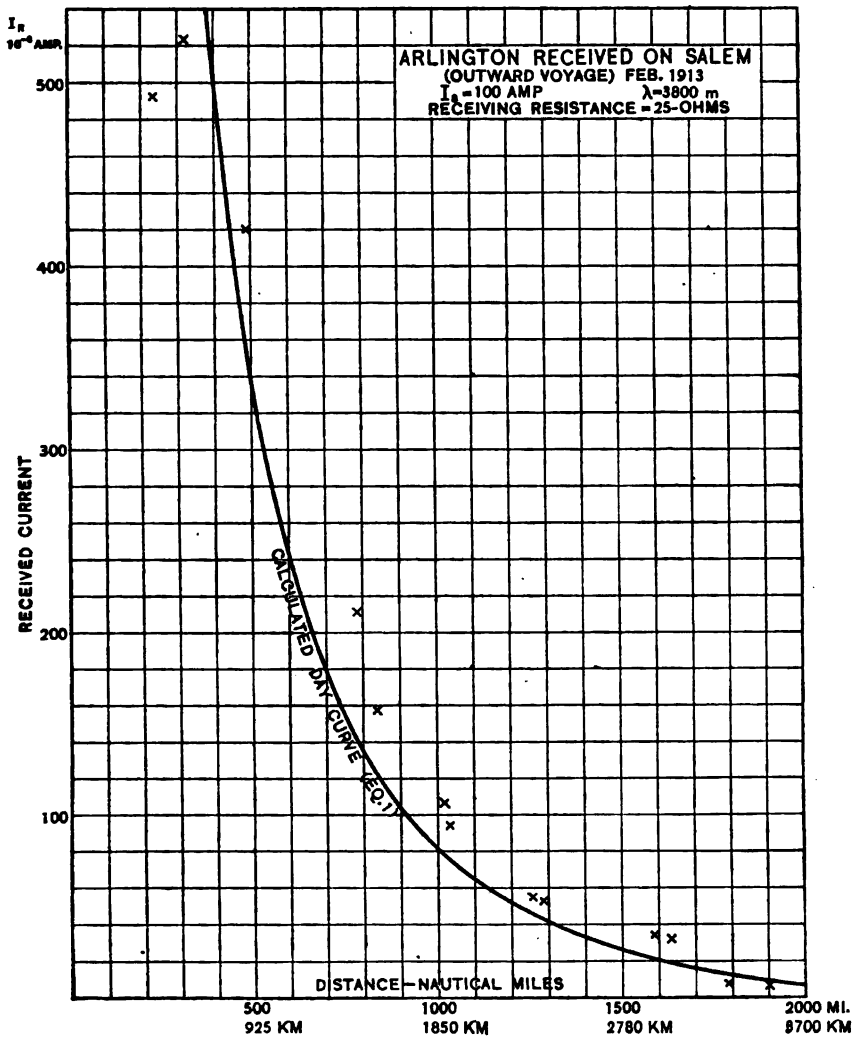


FIG. 1

measurements made by the shunted telephone method on the electrolytic detector in exactly the same way as in the Brant Rock experiments, except that on account of the increased sensitivity of the telephones, the least audible antenna current was

taken as 7 microamperes through 25 ohms, instead of 10 microamperes. The observer was Mr. Lee, who also took the most important observations during the Brant Rock experiments. The curve of the figure is calculated from equation 1 or from Tables 16 and 16a of the report ¹⁶ on the Brant Rock work. Considering the difficulties of taking the measurements, and the assumption of a constant receiving resistance at all wave lengths (see p. 70, this article), the agreement between the calculated and observed values is excellent. It is especially to be noted that the signals became inaudible at almost the exact distance indicated by equation (1). The agreement is better than could be expected and must be looked upon as to some extent accidental.

Observations were made also during the return voyage from Gibraltar. Here the observed values lie considerably lower ¹⁷ than those taken during the outward voyage. They are, in fact, lower than any series which has been observed in our experiments. The two sets of observations are given in Fig. 2, the outward voyage values being indicated by crosses, and those of the return voyage by circles. The dotted curve in the figure gives the values calculated from the theoretical equation (4), but assuming the effective sending height of the Arlington antenna to be 61 m, as indicated approximately by the received current observations at the Washington Navy Yard.

In equation (1) and Fig. 1, the resistance of the receiving system is arbitrarily taken as 25 ohms. The actual receiving resistance of the Salem in the tests with Arlington at a wave length of 3800 m amounted to 50 ohms, distributed as follows: Resistance of inductance 25 ohms, antenna and ground 3 ohms, resistance due to coupled secondary for maximum signals 22 ohms. The decrement δ_1 was approximately 0.05, and δ_2 was 0.14. In the Brant Rock experiments the minimum audibility was determined to be $10 \cdot 10^{-6}$ amp in terms of antenna current through 25 ohms resistance. This would give $2.5 \cdot 10^{-9}$ watts in the receiving system. Assuming that the present telephones would give an audible

¹⁶ This bulletin, 7, p. 315; 1911.

¹⁷ The observations during the return voyage were certainly taken much less carefully than during the outward voyage, partly because the official acceptance tests were finished, and partly because the exacting nature of the work over a long period had begun to tell on the strength of the operators.

response to a received current in the antenna of 7×10^{-6} amperes through 25 ohms, the energy required for an audible signal would

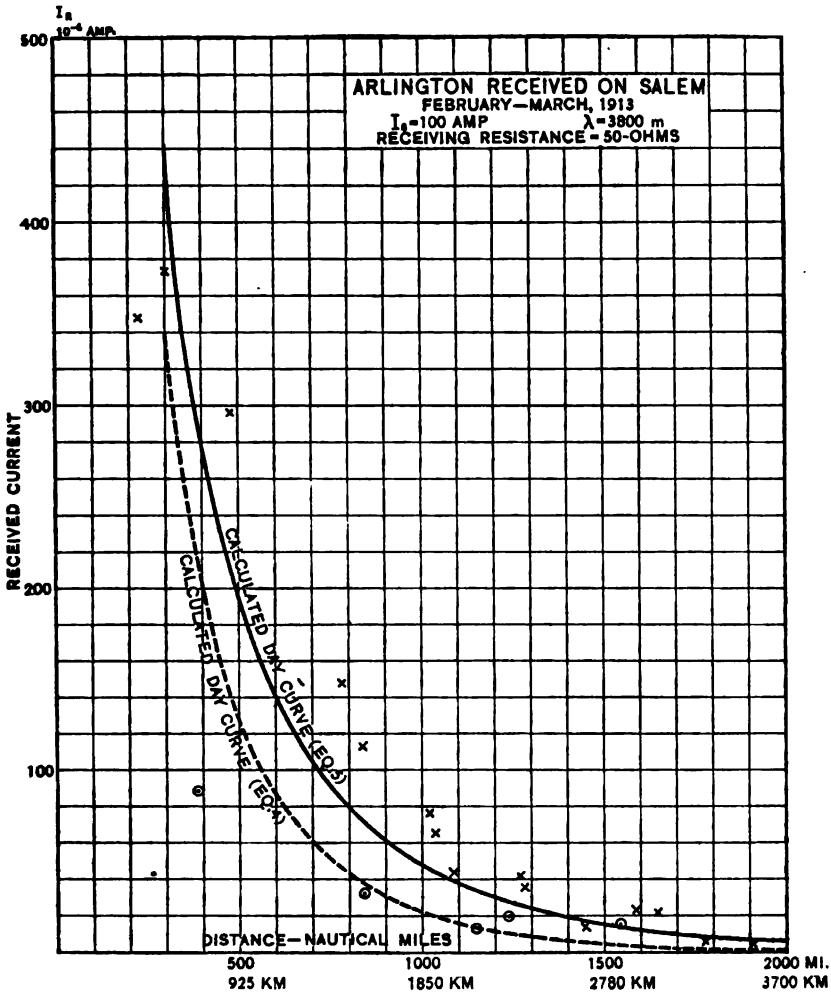


FIG. 2

be 12.25×10^{-10} watts. With this value of the energy required for audibility, and taking 50 ohms as the receiving resistance, the observed values of current in the receiving antenna are shown in

column five of Table 2 and in the observed points of Fig. 2. The dotted curve of Fig. 2 and the third column of Table 2 have been calculated from equation (4).

$$(5) \quad I_R = 377 \frac{h_1 h_2 I_s}{\lambda d R \sqrt{1 + \frac{\delta_1}{\delta_2}}} e^{\frac{-0.0015d}{\sqrt{\lambda}}}$$

In column four of Table 2 and the solid curve of Fig. 2, are given the values of received current as calculated according to equation (5) which is the same as equation (4) except that the scattering

TABLE 2

Arlington Received on the "Salem," February-March, 1913

Distance		Received current 10^{-4} amp.		
Miles	Km	Calculated		Obs.
		Eq. 4.	Eq. 5.	
300	556	335	431	410
400	740	200	278	300
500	925	128	195	225
600	1110	85.2	140	160
800	1480	40.7	79.0	95
1000	1850	20.7	47.6	59
1200	2220	11.0	29.7	34
1500	2780	4.42	15.3	19
2000	3700	1.07	5.65	5.0
2500	4630	0.28	2.20	
3000	5560	0.074	0.89	

term $e^{\frac{-0.0015d}{\sqrt{\lambda}}}$ is replaced by the term $e^{\frac{-0.0015d}{\sqrt{\lambda}}}$ as derived from our Brant Rock experiments (equation (1)). There can be no doubt from these results that the theoretical equation (4) gives values too low to be reconciled with the observations, but that they are in very fair agreement with the semiempirical equation (5).¹⁸

Receiving observations were made also at Arlington with the Salem sending, the received currents at the distances beyond 450 miles (830 km) being measured by the calibrated detector method and the others by thermoelements. During the outward voyage

¹⁸ The currents received at any distance greater than 100 or 200 miles from the sending station often vary from day to day in a ratio of more than 2 to 1, quite apart from experimental errors. For this reason, only the observations beyond 1200 miles have any great weight in the relative validity of equations (4) and (5)

no measurements were made except at 820 and 910 miles (1516 and 1684 km), but on the return voyage a fairly complete series was taken. The wave length used by the Salem was 2000 m, the antenna current on the outward voyage was 26 amperes, and on the return voyage 20 amperes. The observations are shown in Fig. 3, the outward values, reduced to 20 amperes radiation, are shown as crosses and the return observations as circles.

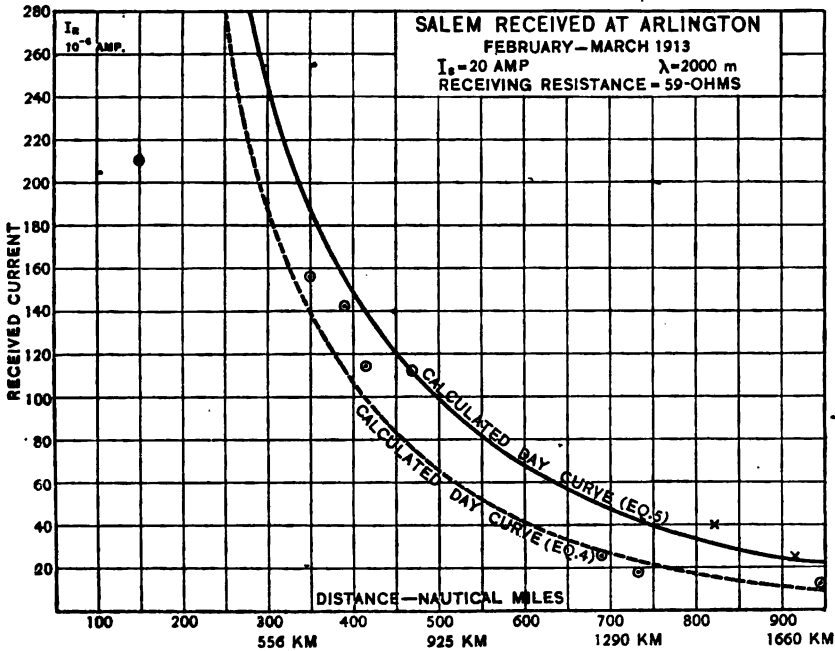


FIG. 3

The solid curve of Fig. 3 represents the calculated values for the received current as taken from equation (5), while the dotted curve is taken from the purely theoretical equation (4). At these distances the differences between equations (4) and (5) are so small that both curves appear to agree fairly well with the observed values.

OTHER OBSERVATIONS

From the many quantitative observations of the high frequency antenna current in sending and receiving made by the Navy Department, a few are collected in the following section.

They are intended to show the relation between the theoretical and observed values and also in some cases to indicate the effect of land absorption, especially as determined by wave length.

In Table 3 are given the data of a series of experiments carried on between the U. S. S. *Florida*, used as a sending station, and the

TABLE 3
U. S. S. "Florida" Received at the Bureau of Standards

λ meters	Received current 10^{-4} amp.		Obs. Cal.
	Obs.	Cal. Eq. 5.	
750	44.8	295	0.15
1000	53.0	222	.24
1200	57.5	177	.33
1500	62.2	132	.47
2000	55.5	86.0	.65
2400	45.0	61.8	.73

$I_s = 20$ amp $d = 130$ miles (240 km) $h_1 = 39$ m. $h^2 = 30$ m.

United States naval radiotelegraphic laboratory, at Washington, used for receiving. The *Florida* during the time of the experiments lay near the entrance to Chesapeake Bay at a distance of about 130 miles from Washington. About two-thirds of this distance lay overland. The third column represents the values of received current calculated for transmission over salt water. The last column of the table which represents the ratio of observed to calculated received current, shows the increase of efficiency of transmission overland with increasing wave length, which agrees at least qualitatively with the theory. The calculated values of received current in the table are derived from the equation (5).

In Table 4 are given data regarding the navy yard stations at Philadelphia and Norfolk, received at the Bureau of Standards in autumn, and also Arlington received at St. Augustine in winter. This last shows how small the ground absorption may be at this distance for wave lengths of approximately 4000 m, being only a few per cent greater than that which would be expected over salt water.

TABLE 4

Sending station	Receiving station	λ meters	I_a amp.	Distance		h_1 meters	h_2 meters	R ohms	Received current 10^{-8} amp.		Obs. Cal.
				Miles	Km				Obs.	Cal. Eq. 5.	
Philadelphia navy yard.	Bureau of Standards.	1000	10	100	185	39.0	30.0	69	76.8	239	0.32
Norfolk navy yard.	do.....	1000	10	127	235	52.0	30.0	69	78.4	231	.34
Arlington spark.	St. Augustine	4100	90	530	980	*61	43.0	64	130.0	158	.80
Arc.....	do.....	4100	48	530	980	*61	43.0	53	85.0	106	.79

* λ corrected from short-range observations.

COMPARISON OF ARC AND SPARK-SENDING APPARATUS

The question of the transmission efficiency of continuous and damped oscillations has caused much discussion between the adherents of the two methods. Several attempts have been made to settle this question by experiment, but over the moderate distances employed until recently no difference has been observed. In order to extend the observations to greater distances, two sets of experiments have been carried on from the Arlington station. For the first (winter of 1912-13) a 30-kw arc operated with 500-volt direct current was procured from the Federal Radiotelegraph & Telephone Co. At a wave length of 4100 m the arc gave an antenna current of approximately 50 amperes. At that time the regular spark-sending set of the station, operated at 1000 sparks per second, produced an antenna current of from 90 to 100 amperes. Careful measurements of received current were made at St. Augustine for the purpose of comparing the relative efficiency of the two methods of transmission. The results given in Table 4 indicate that at this distance, 530 nautical miles (980 km), no certain difference exists. These results were verified roughly by the shunted telephone method, using the slipping contact detector¹⁹ at New Orleans and at Key West, both stations being approximately 900 nautical miles from Washington.

¹⁹ J. Wash. Acad., 1, p. 8, 1911.

Shortly afterwards, observations were made at the naval station at Colon, 1780 nautical miles from Arlington. During the two days on which observations were made, while both arc and spark signals were heard at night, the arc only was heard in the daytime. These observations indicated that at this distance the efficiency of transmission of the continuous waves was greater than that of the damped waves. During the voyage of the *Salem* to Gibraltar and return, which has already been mentioned, additional observations were made which indicated that the arc with half the antenna current, produced signals of practically the same intensity as the spark at 1500 to 2000 miles (2800 to 3700 km), as measured on the slipping contact detector, and actually seemed superior on the Fessenden heterodyne. Messages were continuously received with both arc and spark in the daytime up to 2100 miles (3900 km). Occasional signals were heard much farther, the arc being heard on one day in the daytime even in the harbor of Gibraltar. Both arc and spark were heard at night at all times during the voyage.

In order to make a comparison of the relative desirability of arc and spark transmission under summer conditions, a second series of observations was carried on between the Arlington station and Colon during the months of July and August, 1913. This time was chosen for the test on account of the fact that the signals are weakest at this period of the year, and at the same time the atmospheric disturbances are the strongest, so that the test may be considered as carried on under the most trying conditions.

For this work a 100-kw Poulsen arc belonging to the Universal Radio Syndicate was available for comparison with the regular rotary gap set of the Arlington station. The regular experiments began on July 25. The distance from Arlington to Colon is 1780 nautical miles (3300 km). From the formula deduced from the Brant Rock experiments, the Arlington signals, at a wave length of 4000 m, should be faintly audible at this distance, using a sensitive crystal detector and an antenna 180 feet high. As a matter of fact, the signals are just below audibility with ordinary detectors, as is shown from their strength on the more sensitive slipping contact detector. This fact may be due to the passage of the waves

over Cuba, or to other conditions of transmission in this portion of the world.

The receiving work at Colon was done by Chief Electrician Meneratti, assistant at the naval radio laboratory. The receiving apparatus used consisted of a Federal receiving set, which is especially efficient at the longer wave lengths, a slipping contact detector, and a Fessenden heterodyne. The regular antenna of the Colon station, 180 feet (55 m) high and of about 0.0025 μ f. capacity, was used for the work.

The arc signals were sent out from Arlington at wave lengths of 4000, 5000, 6000, and 7000 m. Two wave lengths were used with the spark, 3500 m and 2500 m. The latter, however, proved so unsatisfactory at this distance that its use was abandoned after the first few days.

On account of the continuous atmospheric disturbances quantitative comparisons were of little value. The following table, Table 5, gives the number of schedules sent at the various wave lengths, and the corresponding number received.

TABLE 5
Comparison of Arc and Spark

	Wave length	Sending current amp.	Total schedules		Schedules heard	
			Day	Night	Day	Night
	m					
Spark.....	3500	104	9	0	7	0
Arc.....	4000	52	9	4	7	4
Arc.....	5000	60	0	4	0	4
Arc.....	6000	70	6	0	2	0
Arc.....	7000	78	3	7	3	7

The table shows that the best results were obtained with the arc at 7000 m, every schedule being successfully received. The same is true of the 5000-m arc waves, but in this case all the work was done at night, which prevents its being properly compared with the other schedules. The 4000-m arc and the 3500-m spark waves, which may be fairly compared, were received with the same degree of regularity and were of approximately the same strength as

compared on the slipping contact detector, although the spark antenna current was double that of the arc. In this connection it must be remembered, as will be explained later, that while 80 per cent of the spark schedules were weakly audible on the heterodyne or slipping contact, practically none of the messages were readable. It appears from Meneratti's report that 50 per cent of all the arc messages sent at the various wave lengths, that is, 65 per cent of the arc schedules heard at all, would have been completely readable by double repetition. The very poor showing of the 6000-m wave, compared with the 4000 and 7000-m waves, is probably due to a defect in the receiver at this wave length.

One of the most interesting portions of the work was the study of the behavior of the slipping contact detector and heterodyne under the conditions of continuous atmospheric disturbances at Colon. The reports indicate that the heterodyne is somewhat more sensitive than the slipping contact, but that the difference is not very great. With spark signals the note produced by both is unmusical and difficult to distinguish from the atmospherics, and, as Meneratti remarks, both are inferior to a good crystal detector in receiving weak 500-cycle signals through continuous atmospherics. With arc signals, however, the case is entirely different. Here the slipping contact detector produces the same rustling sound as in the case of the spark, but the heterodyne produces a musical note of any pitch found most suitable for reading through the disturbances.

DISCUSSION OF RESULTS

The most important question which these experiments seek to solve is whether or not the theoretical formula (equation (2)) represents the observed facts of radio transmission. The first, or Hert-zian, term of this formula agrees with the observations at short distances, but it is found that, for most of the land stations at least, the length of the equivalent oscillator is considerably less than twice the height of the antenna. The formula as a whole does not give satisfactory results at great distances, the scattering term apparently producing a diminution in electric intensity considerably greater than the observed values. In the Arlington-Salem experiments, at a distance of 3700 km, the strength of

received current as calculated from the formula was only one-fifth of that actually observed, and would have reduced the signals below audibility at a distance of about 2600 km, while in reality they remained audible at 3700 km. A semiempirical expression for the received current was made up of a combination of the Hertzian portion of the theoretical formula with the absorption term from the purely empirical Brant Rock formula (equation 1). This expression, shown in equation 5, is in good agreement with the observations up to 3700 km at a wave length of 3800 m.

At present our observations on the transmission of different wave lengths over great distances are too meager in number to settle the question of the relation between the attenuation of the signals and the wave length. It is certain, however, that the attenuation even over sea water is very much decreased as the wave length is increased. It seems possible that, while the theoretical formula does not represent the facts at great distances, it would do so if all the energy withdrawn from the wave train, as represented by the scattering term, were actually lost. There is strong evidence,²⁰ however, that a portion of it again reaches the surface of the earth either by means of reflection or possibly refraction in the upper layers of the atmosphere. This reinforcement is undoubtedly very strong at night, producing the so-called night effects with their phenomenal distances of transmission. It is also probable that it plays an important part in the day time, increasing the transmission range, especially in winter, and also producing the irregularities in intensity frequently observed. If this be true, an additional term ought to be added to the theoretical formula. The experiments at moderate distances over land show a marked increase in ground absorption with decreasing wave length, at least qualitatively in accordance with the theory. For distances up to 2000 km, provided a wave length of more than 4000 m is used, ground absorption in most cases seems to nearly disappear, so that the transmission is almost identical with that over salt water. This is clearly shown at a distance of 980 km in the Arlington-St. Augustine experiments. (See Table

²⁰ J. Washington Academy, 8, p. 284, 1913; *Jahrbuch der drahtlosen Telegraphie*, 7, p. 306, 1913; J. Washington Academy, 8, p. 326, 1913.

4.) The energy of overland night signals at moderate wave lengths appears to be transmitted mostly through the upper atmosphere, as the nature of the ground seems to have practically no influence.

The comparisons made of the efficiency of arc and spark transmission have indicated that, for distances of the order of 3700 km or more, continuous oscillations are on an average superior. The evidence is not complete enough to prove that this superiority always exists. It is apparently connected in some way with the reinforcement of the signals from the upper layers of the atmosphere, and is subject to the vagaries of this portion of the received energy. The indications seem to be that the superiority of the continuous oscillations is greater in winter than in summer.

U. S. NAVAL RADIO LABORATORY,
WASHINGTON, April 1, 1914.

MEASUREMENTS ON STANDARDS OF RADIATION IN ABSOLUTE VALUE

By W. W. Coblentz

One of the chief needs in the measurement of radiant energy is a convenient standard against which the radiometer may be calibrated. Another desideratum is a simple radiometer the receiver of which is continuous (that is, has no openings or perforations in it), and which will thus intercept all the radiant energy within a given area. The surface of such a receiver may be rendered completely absorbing, to within 1.5 to 2 per cent, by smoking it. Then, if the flux of energy at a given distance from the standard radiator and the area of the radiometer exposed are known, it is an easy matter to calibrate the instrument in such a manner that one experimenter's work can be reproduced by another. As a convenient and very sensitive radiometer, the bismuth-silver thermopile with such a continuous receiver has been found to fulfill the requirements, and the latest developments in this line will be given in a forthcoming paper. In the present paper only the standards of radiation will be considered.

THE HEFNER LAMP

One of the earliest attempts to establish an absolute standard of radiation was made by Ångström¹ who determined the radiation from the Hefner lamp. In his earliest work he placed a screen, having an opening of 14 by 40 mm, at a distance of about 10 cm in front of the flame, which was kept burning at a height of 40 mm. Unfortunately, in his subsequent papers no further reference is made to this diaphragm, and the general custom now seems to prevail to use the Hefner lamp without a diaphragm, just as it is used in photometry. The result is that the radiation

¹ Ångström: Wied. Ann., 67, p. 633, 1899; Phys. Zs., 8, p. 257, 1902; Phys. Rev., 17, p. 302, 1903.

from the nonluminous gases above the flame adds about 18 per cent to the radiation received through the 40 by 14 mm slit, as defined by Ångström. Hence, the calibrations of radiometers made in terms of the Hefner lamp without the diaphragm are in error by about 18 per cent.

The value of the intensity of the radiation (presumably passing through the 40 by 14 mm slit, although no mention is made of it in the later measurements) as determined by Ångström with an electrically compensated pyrhelimeter, at a distance of 1 m from the lamp, is 21.5×10^{-8} g-cal. per square centimeter per second. No correction was made for reflection. Applying this correction (2 per cent) makes Ångström's value 21.9×10^{-8} g-cal. per square centimeter per second.

A new determination of this constant has recently been made by Gerlach² with a modified form of Ångström pyrhelimeter. He limited the radiation from the Hefner flame by placing a diaphragm having an opening 50 by 14 mm, at a distance of 10 cm from the flame. The lower edge of the opening in the diaphragm extended about 5 mm below a horizontal line through the top of the tube holding the wick, and, hence, extended 5 mm above the flame as measured by Ångström. He examined amyl acetate from various sources, and used different lamps. Under these conditions he found values of 21.7 to 22.7×10^{-8} g-cal. per square centimeter per second for the radiation at a distance of 1 m from the Hefner lamp. The predominating values are 22.5 to 22.6×10^{-8} g-cal. per square centimeter per second which, when corrected by 2 per cent for loss by reflection from the receiver, gives a mean value of about 23.0×10^{-8} g-cal. per square centimeter per second. In view of the fact that Gerlach's determinations were made with an instrument which gave him a high value for the constant ($\sigma = 5.90 \times 10^{-12}$ watt. cm^{-2} deg.⁻⁴) of total radiation of a black body, the accuracy of these measurements remains to be determined. It also remains to be decided whether it is worth while to attempt to attain a higher accuracy, for it is known that the candlepower varies with the atmospheric humidity, and it is probable that the total radiation also varies with the humidity.

² Gerlach: *Phys. Zs.*, 14, p. 577; 1913.

The variation in humidity has, no doubt, the greatest effect by absorbing infra red radiation. Gerlach found no marked difference in his values for different lamps and for pure amyl acetate.

In view of the fact that the Hefner lamp is a convenient standard, and in some cases is sufficiently accurate when properly used, it was compared directly against a black-body radiator which is being used in the determination of radiation constants. The standard incandescent lamps to be mentioned presently and the flame standards were compared on the same day. The absolute value of the radiation, as given, is based upon the constant of total radiation $\sigma = 5.7 \times 10^{-12}$ watt. cm^{-2} deg^{-4} , which is practically the mean value of the best present-day determinations of this constant.

On account of the high sensitivity of the radiometers now available, which gives excessively large deflections when the standard of radiation is at a distance of 1 m, the present measurements were made with the radiometer situated at a distance of 2 m from the center of the wick tube of the lamp. The inverse square law is then applied to obtain the value at the conventional distance of 1 m, on the assumption that the atmospheric absorption is negligible and that the opening in the diaphragm represents a point source. Under these conditions the radiation of the Hefner lamp, with and without a diaphragm (at a distance of 10 cm from the flame), is given in Table 1. It is desirable, however, to make the measurements at a distance of 2 m.

TABLE 1
Radiation from Hefner Lamp and Standard Sperm Candle

Opening in diaphragm	Radiation per cm^2 at 2 m		Radiation in g-cal. per cm^2 per sec. at 1 m
	Watt	Gram calorie per second	
14 by 40 mm	23.1×10^{-6}	5.5×10^{-6}	22.0×10^{-6}
14 by 50 mm	24.2×10^{-6}	5.8×10^{-6}	23.2×10^{-6}
No diaphragm	27.2×10^{-6}	6.5×10^{-6}	26.0×10^{-6}
Sperm candle: No diaphragm	30.5×10^{-6}	7.3×10^{-6}	29.2×10^{-6}

In the present work the diaphragm, with an opening 14 by 50 mm, was placed at a distance of 10 cm from the flame. The lower edge of the opening was placed on a level with the top of the German-silver tube which holds the wick. The upper edge was formed by a movable cover which could be lowered, thus forming openings 50, 45, 42, and 40 mm in height. The center of the receiver was placed at the same height as the center of the opening in the diaphragm.

The radiation passing through the opening 42 mm in height was about 0.9 per cent greater than that passing through the opening 40 mm in height. Using no slit, the radiation (observed at 1.2 m from the flame) was 18 per cent higher than that observed through the slit opening of 14 by 40 mm. The precision attained in these preliminary measurements was not so high as in subsequent work. The precision attained in the final measurements may be judged from the three sets of measurements of the radiation from the flame (having no diaphragm) made on different days, the lamp having been reset in the meantime. The departure of these three values (26.09, 26.00, and 26.03; mean value = 26.04×10^{-8} g-cal. cm⁻² sec.⁻¹ at 1 m) from the mean is far less than is ordinarily found in radiometric work. A similar series of observations made in July, 1913, having the lamp at 1.2 m, gave a value which was over 2 per cent higher.

These measurements were made in the winter when the moisture content in the atmosphere was low. Owing to the variable absorption of atmospheric water vapor in the infra-red, the Hefner lamp can not be considered a standard for high precision in standardizing radiometers. As already mentioned, the present measurements were made at a distance of 2 m, since that is a convenient distance from sensitive radiometers. Because of atmospheric absorption in the infra-red and of the fact that the diaphragm opening does not represent a point source, the inverse square law can not be rigorously correct, so that if measurements are made at, for example, 2 m, then reduced to a distance of 1 m, the value thus found is smaller than the one observed directly at a distance of 1 m. For example, the radiation from this lamp with a diaphragm opening of 14 by 50 mm, determined seven months

ago (July, 1913), at a distance of 1.2 m gave a value of 24.5×10^{-6} g-cal. cm^{-2} sec^{-1} at 1 m. The radiation through the 14 by 40 mm opening was then 23.3×10^{-6} g-cal. cm^{-2} sec^{-1} . These absolute values determined at the shorter distance are, respectively, 5.6 and 5.9 per cent higher than those observed at 2 m and reduced to the conventional distance of 1 m.

Gerlach's data show a similar deviation from the inverse square law. His values, reduced to a distance of 1 m, are of the order of 23.1×10^{-6} g-cal. when the lamp stood at 0.86 m. from the receiver, and of the order of 21.8×10^{-6} g-cal. when the lamp was distant 2 m. This is a systematic difference of about 5 per cent in his results, which is in agreement with present observations. That it is not greater is no doubt owing to the use of the diaphragm having an opening 14 by 50 mm, which shields the thermopile from the hot gases above the flame, for the radiation from these hot gases (CO_2 and water vapor), situated a short distance above the luminous portion of the flame, would suffer most by absorption in traversing the 2 m of air.³

In order, therefore, to give a reasonably accurate statement of the sensitivity of a radiometer, in terms of the radiation from a flame standard of radiation it is important to use the lamp as specified. Using a diaphragm with an opening 14 by 50 mm, situated at a distance of 10 cm from the flame, the value of the radiation of the Hefner lamp may be taken to be 23×10^{-6} g-cal. per square centimeter per second at 1 m without reference to the humidity, when an accuracy not higher than 5 to 6 per cent is desired. If a more reliable measurement is to be made, a seasoned incandescent lamp, which has been calibrated against a black body, should be used.

THE STANDARD SPERM CANDLE

The so-called standard sperm candle is often employed in radiation sensitivity tests, but its use is to be discouraged because of the great fluctuations in its burning. The mean value for different candles was found to be fairly constant, but in any one candle the maximum to minimum fluctuation in radiation varied by 18 to 20

³ For data and references to the great opacity of CO_2 and water vapor in the infra-red, see this Bulletin 7, p. 679; 1911.

per cent. The total radiation at a distance of 2 m from the radiometer was observed for over an hour. No diaphragm was used in front of the flame. It was easy to see when the burning was far above or below "normal." The mean value of the galvanometer readings was taken when the deflections were fairly constant. The average radiation from a standard sperm candle, at a distance of 1 m was found to be 29×10^{-8} g-cal. per square centimeter per second. The radiation from the standard candle is therefore about 12 per cent higher than that from the Hefner lamp. This is a little higher than the photometric ratio, as one would expect, since the red-hot wick contributes but little light but it emits infra-red radiations.

CARBON INCANDESCENT LAMP STANDARDS

The great utility of a seasoned carbon incandescent lamp as a photometric standard is well recognized; and such a lamp has every desideratum of a standard of radiation, when calibrated against a black body as the primary standard of radiation. If a series of incandescent lamps be calibrated against a black body and preserved by the national laboratories, it will be a simple matter for an experimenter to have the radiation from his standard incandescent lamp certified in terms of these lamps, thus obtaining a calibration in absolute value. With such a lamp higher precision may be attained than is possible with flame standards. The radiation, which is transmitted by the glass bulb of the lamp, being of wave lengths less than 3.5μ , is affected but little by variations in atmospheric humidity, and hence no correction for atmospheric absorption will be necessary. The radiometer surfaces are sufficiently nonselective in their absorption, so that a more reliable calibration is to be expected from an incandescent lamp whose spectrum terminates at 3.5 to 4.0μ , than from any form of radiator which emits an appreciable amount of radiation of wave lengths greater than 4μ . No diaphragm is used in front of the lamp, which has lines etched upon it to insure proper orientation.

The main precautions to be taken in using a radiation standard are: (1) To have a black cloth about 1 m to the rear of the lamp to prevent reflection of radiation from the wall; (2) to observe

the amount of radiation from the walls to the radiometer (or from the radiometer to the walls) when the shutter is raised from in front of the lamp before it is lighted; and (3) to operate the lamp about 10 minutes to thoroughly warm the inner parts before making readings.

The comparison of the incandescent lamps against a black body is not made without some difficulties, but from the results given in Table 2 it will be noticed that a high precision is attainable. In fact, the deviations from the mean value are due chiefly to inaccuracies in the determination of the galvanometer sensitivities on different days. Using a potentiometer device this inaccuracy would be eliminated.

TABLE 2

Observations on Incandescent Lamp C₁, with Thermopiles Calibrated Against a Black Body

[The energy is given in watts per mm² $\times 10^{-8}$ and the per cent deviation, "dev.," from the mean value]

Uncorrected amps.	Pile No. 23 Calibration July 9, 1913 Observations July 9, 1913		Pile No. 21 Calibration July 9, 1913 Observations July 9, 1913		Pile No. 25 Calibration July 22, 1913 Observations July 22, 1913		Pile No. 25 Calibration July 22, 1913 Observations July 31, 1913		Mean value
	Watts $\times 10^{-8}$	dev.	Watts $\times 10^{-8}$	dev.	Watts $\times 10^{-8}$	dev.	Watts $\times 10^{-8}$	dev.	
0.45					115.8	+0.13	115.5	-0.13	115.65
.4385	109.75	+0.69	108.25	-0.69					109.00
.42	100.50	+ .76	99.27	- .47	99.40	- .34	99.77	+ .03	99.74
.40	89.78	+ .60	88.96	- .22	88.76	- .42	89.23	+ .05	89.18
.38	79.96	+ .11	80.00	+ .16	79.63	- .30	79.88	+ .01	79.87
.35	67.37	+ .52	67.03	+ .01	66.58	- .66	67.08	+ .09	67.02
.30							48.23		48.23

The method of observation consisted in exposing the thermopile alternately to a black body radiator and to the standard lamps. In order to determine the "constants" of the thermopile the distance from the black body was varied; water-cooled shutters and diaphragms of known apertures were used; the black body was heated at different temperatures from 700° to 1200° C, and all the rules were observed for the operation of such a radiator. The constant of radiation was taken to be $\sigma = 5.7 \times 10^{-12}$ watts per square centimeter, and the value of 1 mm deflection (the

"constant" of the thermopile used) was determined in terms of radiation in absolute value for a given galvanometer sensitivity. For example, using a galvanometer sensitivity of $i = 5 \times 10^{-10}$ ampere, the "constant" of thermopile No. 10 was 1 mm deflection $= 4.15 \times 10^{-8} \pm 0.03$ watt, and of thermopile No. 21, 1 mm deflection $= 6.28 \times 10^{-8} \pm 0.05$ watt. Usually the comparison of the thermopile was made against the black body and the incandescent lamp on the same day, before the galvanometer sensitivity and other conditions could change. In the later observations, Table 2, in which greater care was taken in determining the galvanometer sensitivity, a precision of a few parts in one thousand was attained; and if there were a demand for it, a still higher accuracy could be attained by taking certain minor precautions not ordinarily observed.

The intercomparison of two incandescent lamps is an easy matter. For example, after a lapse of about seven months two standard incandescent lamps were intercompared, the one lamp having been used considerably in the meantime. The lamps were operated on 0.4 ampere, on which current the ratio of their energy emission, as read from the calibration curves, was supposed to be 1.079. The ratio of the energy radiated, as observed with a thermopile (in air, no window, area exposed 1.833 by 14.415 mm), was 1.082, which is a deviation of 0.3 per cent. That the precision attained was not higher was owing to the fact that the measurements were made on a windy day, when air currents caused unsteadiness in the deflections; and also owing to a difference in the temperature of the shutter (in front of the lamp), the thermopile, and the walls of the room, which affected the deflections by 0.12 cm, with an uncertainty of 0.02 to 0.03 cm. Subsequent to this test about a dozen incandescent lamps were intercompared radiometrically. The values of energy emitted were found in agreement by 1 to 3 parts in 1000 with the direct calibration made six months ago, which was as close as the calibration curves could be read.

SPECIFICATION OF RADIOMETER SENSITIVITY

The specification of the sensitivity of a thermopile in terms of "microvolts per microwatt" of radiant power, or a similar notation, is not complete. In a forthcoming paper it will be shown that the

joint sensitivity of a thermopile and galvanometer to radiation is not seriously decreased (this decrease amounts to about 5 per cent) by having the external resistance twice as great as the internal resistance; a greater difference will hardly occur in practice. It will be shown, also, that the radiation sensitivity of the thermopile is as much a question of nicety of construction as it is of the number of thermoelements, and of the thermoelectric power per element. It seems sufficient, after specifying the current sensitivity of the Thomson galvanometer, to state the deflection produced per microwatt of radiant power incident upon the receiver of specified area. This will be necessary if calibrated incandescent lamps be used. In this manner the thermopile serves merely as an intermediary in comparing the intensity of a radiation ("light") stimulus with that of a standard of radiation.

The custom of specifying the radiation sensitivity in terms of the total radiation received from a standard flame per square centimeter of area of the receiver exposed at a distance of 1 m is useful and, on the assumption that the constant of total radiation of a black body is $\sigma = 5.7 \times 10^{-12}$ watt cm^{-2} deg^{-4} , the following relations are given:

Source	Radiation
1 sperm candle.....	29 microcalories per centimeter.
1 Hefner unit.....	26 microcalories (no diaphragm).
1 Hefner unit.....	23 microcalories (diaphragm with opening 14 by 50 mm).
1 microcalorie.....	0.034 sperm candle.
	0.0385 Hefner unit (no diaphragm).
	0.043 Hefner unit (diaphragm with opening 14 by 50 mm).

In conclusion, it is desirable to emphasize the importance of specifying the intensity of a radiation stimulus in accurate units so that an experimenter's work can be repeated. For example, in photo-electric work, in stimuli applied to the eye, in experiments on the variation of sensitivity of selenium with intensity of the stimulus, in photostimuli as affecting plant growth, and in photo-chemical reactions in general it is desirable to specify accurately the mechanical equivalent of the stimulus. By using a receiver, having a known opening, which is completely filled by the stim-

ulus radiations, it is a simple matter to expose the thermopile to a standardized lamp, and by this comparison to determine the intensity of the stimulus in absolute measure to a high degree of accuracy. In this manner a better agreement will be attained between theory and experiment, and radiometry may attain a dignity comparable with other lines of investigations.

SUMMARY

In the first part of this paper measurements are given of the radiation from the Hefner lamp and from a standard sperm candle relative to that of a black body. The data are useful for rough comparison of radiometers in absolute measures.

For refined measurements of radiation stimuli a standardized incandescent lamp is recommended for calibrating the radiometer. In the second part of this paper tabulated data are given, showing the precision attained in standardizing such an incandescent lamp against a black body by means of three thermopiles having widely different constants.

WASHINGTON, January 16, 1914.

SUPPLEMENTAL NOTE

During the past few months a series of preliminary measurements were made on the constant of total radiation (" σ ") of a black body by means of a modified form of Ångström pyrheliometer. In view of the fact that this instrument will be described in a forthcoming paper on radiometers, it will be sufficient to say that the device consists of a thin strip of metal which serves both as a heater, and also as a receiver. At a short distance back of the heater-receiver is placed a linear thermopile of bismuth-silver, having a continuous receiving surface of tin. In front of the receiver are jaw slits so arranged that they may be entirely removed, thus exposing the entire width of the receiver to radiation. These slits define the width (2.5 to 5.5 mm) of the receiver which is exposed to radiation. The total length of the receiver is about 30 mm between the points where it is attached to the heavy copper terminals. Potential terminals of platinum wire 0.005 mm (also 0.025 mm) in thickness are attached at a distance of about 3 mm from the ends of the receiver. The length of the receiver which is exposed to radiation is determined by the distance (23 to 24 mm) between the potential terminals, or by slits across the ends of the receivers, with their edges directly over these potential terminals. No difference (1 part in 600 or more) could be detected in the galvanometer deflections with and without these slits across the ends of the receiver. Hence, most of the measurements were made without the slits at the ends. Measurements were made with different amounts of overlapping of radiation along the sides of the receivers.

The method of observation consists in exposing the receiver to radiation and noting the galvanometer deflection, the sensitivity of the radiometer being such that a change in temperature of $0^{\circ}.1$ in the black body produced a change of 1 mm in the deflections. The receiver is then heated by passing a sufficient current through

it to produce very closely the same deflection as was caused by the absorption of radiant energy. The amount of electric current flowing through the receiver heater is determined by measuring the drop in potential across a standard 1 ohm resistance. The voltage across the potential terminals is also measured. A Leeds & Northrup type K potentiometer with 0.1 shunt is used in measuring these voltages. From these two measurements the energy input is easily determined.

Two kinds of receivers were used. Those of "Therlo" (1 and 3) were 0.007 to 0.008 mm in thickness. They were painted with a mixture of lampblack and platinum black and then smoked, as described in a previous paper.⁴ The reflecting power of lampblack was taken to be 1.3 per cent, which value was applied to obtain the data herewith presented. The platinum receivers (Nos. 2 and 4) were made of the thinnest material used in bolometers. Their thickness was probably less than 0.1 that of the "Therlo." They were covered electrolytically with platinum black, the reflecting power (1.4 to 1.8 per cent) of which was estimated by comparison with the samples of which the reflecting power had previously been determined.

With these instruments four series of measurements were made on the standard incandescent lamps. Measurements were, of course, made also on the black body, which was heated to about 1000° C.

The data are given in Table 3, the distance from the lamp being 2 m, as usual. The mean value (89.0) for lamp C₁, operated on 0.40 ampere, is very close to the mean value (89.18) of the previous measurements which were made on the assumption that the value of the constant of total radiation is $\sigma = 5.7 \times 10^{-12}$ watt cm⁻² deg⁻⁴. Using a more probable value of $\sigma = 5.65 \times 10^{-12}$ watt cm⁻² deg⁻⁴, the direct measurements of lamp C₁, on 0.40 ampere (see Table 2) would be 88.38×10^{-8} watt per square millimeter. These lamp standards of radiation may, therefore, be considered established with a fair degree of accuracy (0.5 per cent) without considering the value of the radiation constant, which probably will be found to be of the order of $\sigma = 5.65 \times 10^{-12}$ watt cm⁻² deg⁻⁴, or even a

⁴ This Bulletin, 9, p. 283, 1913.

trifle lower than this value. A series of measurements made on this lamp (C_1 on 0.40 ampere), with an instrument constructed for nocturnal radiation work, gave a value of 89.8. In this instrument the thermopile receivers are in contact with the manganin heater-receiver.

TABLE 3

Direct Measurements in Absolute Value of the Radiation in Watts per mm^2 at a Distance of 2 Meters from Standard Lamp C_1 When Operated on 0.4 Amp. (See Table 2)

Date	Receiver Area in mm^2	Correction applied for reflection (Per cent)	Radiation watts $\times 10^{-8}$	Deviation from mean value	Remarks
May 15, 1914.....	No. 2..... 3.192×24.354 = 77.738	1.4	89.24	+ .24	Pt. Black.
May 21, 1914.....	No. 1..... 2.150×23.092 = 49.649	1.3	88.56	- .44	Seet.
May 23, 1914.....	No. 3..... 4.990×24.910 = 124.301	1.3	89.47	+ .47	Seet.
June 2, 1914.....	No. 4..... 5.508×26.565 = 146.321	1.8	88.95	- .05	Pt. Black.
June 6, 1914.....	No. 4..... 5.49×26.565 = 145.842	1.3	88.80	- .20	Pt. Black. Smoked.

Mean value = 89.00

The measurements on the flame standards, having been made at the same time as those on the incandescent lamps, will not require revision, according to these direct measurements, for they are probably already a trifle high, owing to a possible systematic error which was overlooked in the discussion on a previous page. In the writer's opinion the values given herewith are as accurate as any that would be obtained on further measurements, which the flame standards do not deserve. With reference to a possible systematic error in the direct comparisons with the thermopiles, it is to be noticed that in this method of calibration the thermopiles were placed at a distance of 50 to 75 cm from the black body.

The galvanometer deflections would, therefore, be too small, owing to atmospheric absorption. The "constant" of the thermopile would, therefore, be too large, and the measurements of the radiation from the lamps would be too large. All the measurements, however, are in excellent agreement, showing that whatever the systematic errors were they were eliminated, at least within the limits of errors in making the observations.

When this investigation was undertaken there were two groups of observations on the constant of total radiation, the mean value ⁵ of which was closely $\sigma = 5.7 \times 10^{-12}$ watt cm⁻² deg⁻⁴.

Among the high values are the measurements of Gerlach ⁶, who used a radiometer somewhat similar to the one employed in the present measurements, except that he did not have the potential terminals placed upon the receiver. His value is $\sigma = 5.9 \times 10^{-12}$ watt cm⁻² deg⁻⁴.

The mean value of 50 measurements with the instrument as herein described is $\sigma = 5.61 \times 10^{-12}$ watt cm⁻² deg⁻⁴, which is practically the same as the most reliable determinations falling in the aforementioned group of low values. It may be added that the first measurements made with this instrument also gave high values ($\sigma = 6.0$ to 6.3), but after eliminating stray radiations the value decreased to $\sigma = 5.61 \times 10^{-12}$ watt cm⁻² deg⁻⁴.

In these measurements the receiver was situated at a distance of 25 to 35 cm from the water-cooled diaphragm, having an opening 4.5 mm in diameter, which was placed before the black body. The space between the receiver and the diaphragm was inclosed and kept dry with phosphorus pentoxide.

WASHINGTON, June 24, 1914.

⁵ See the writer's summary in *Jahrb. Radioaktivität und Elektronik*, 10, p. 340; 1913.

⁶ Gerlach: *Ann. der Phys.*, (4) 88, p. 1; 1912.

THE KOEPSSEL PERMEAMETER

By Charles W. Burrows

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1. HISTORICAL

The moving coil galvanometer and many other electrical instruments built on the same principle consist essentially of a coil of wire suspended in a magnetic field. This coil experiences a torque which is proportional to the product of the current in the coil and the component of the magnetic field in the plane of the coils. In the instruments just mentioned the magnetic field is constant and the current varies. The deflection due to the torque thus becomes a measure of the current strength.

Instead of using a constant magnetic field, we may maintain a constant electric current through the moving coil and use this system for the measurement of the magnetic field. If this magnetic field is due to an electromagnet, the magnitude of the field depends upon the magnetomotive force applied and the material of the magnetic circuit. An electromagnetic system of this kind may therefore be made the basis of an apparatus for the determination of the magnetic properties of iron and steel.

Robinson¹ in the *Electrical World* of February 24, 1894, gave a complete description of a permeameter based on this principle. However, he had not actually built the instrument.

Three days later Koepsel² described before a German electro-technical society substantially the same piece of apparatus, which he had built and was actually using. This apparatus, as later improved by Kath,³ is widely used, both in this country and abroad. It is sometimes called the Siemens and Halske permeameter, from the name of the manufacturer.

Orlich⁴ at the Reichsanstalt determined a number of hysteresis loops with the Koepsel instrument and also by the magnetometer method, using ellipsoidal specimens for this latter test. His data show that at inductions of 15 000 gausses the instrument gives values of the magnetizing force which are too high. All values of the coercive force, as obtained by this instrument, are greater than those of the magnetometer. The shearing curves differ for different materials. Rohr⁵ compares hysteresis data obtained by the Koepsel permeameter with that obtained by the watt-meter method and finds that the values of the Steinmetz coefficient thus obtained are in substantial agreement. The Koepsel apparatus has also been used by Voller,⁶ Gans and Goldschmidt,⁷ Allamet and Brunswick,⁸ and others.

Much of the data on the magnetic properties of iron and steel have been determined with this apparatus. It seems, therefore, well worth while to give the Koepsel permeameter a careful experimental examination with a view to determining its reliability for use in making magnetic measurements.

2. THE KOEPESEL PERMEAMETER

Fig. 1 shows the Koepsel apparatus diagrammatically. The magnetic circuit consists of a semicircular yoke J J with its ends

¹ I. T. Robinson: "A modified instrument for the determination of B-H curves," *Electrical World*, 23, p. 236; Feb. 24, 1894.

² A. Koepsel: Apparat zur Bestimmung der magnetischen Eigenschaften des Eisens in absoluten Maass und directer Ablesung, *E T Z.*, 16, p. 214; Apr. 12, 1894.

³ H. Kath: *E T Z.*, 19, pp. 411-415; 1898.

⁴ E. Orlich: *E T Z.*, 19, pp. 291-294; 1898.

⁵ W. Rohr: *E T Z.*, 19, p. 713; 1898.

⁶ A. Voller: *Hamburg Verh. Natw. Ver.* (3 folge), p. 8; 1900.

⁷ Gans and Goldschmidt: *E T Z.*, 17, pp. 372-374; 1896.

⁸ Allamet and Brunswick: *Electricien*, 16, pp. 187-191; 1898.

joined by the test piece P. The middle of the yoke has a circular gap in which swings the test coil *h* for the measurement of the induction. The system is magnetized by means of a current in a solenoid S, surrounding the specimen. The constants of the

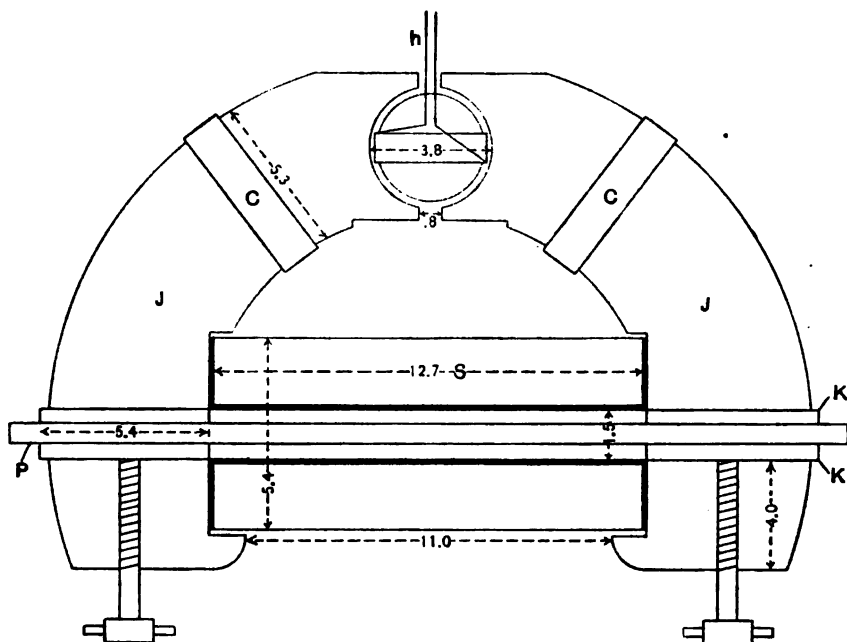


FIG. 1.—Diagram of the Koepsel permeameter

- P Test specimen
- JJ Heavy semicircular soft iron yokes
- K Soft iron bushings
- S Main Magnetizing solenoid
- CC Compensating turns
- h Moving coil

(The dimensions given on the figure are in centimeters.)

instrument are such that the magnetizing force is given by the equation

$$H = 100 I$$

where *I* is the magnetizing current in amperes, and *H* is the magnetizing force in gaussses.

This coil is designed for values of *H* as large as 450 gaussses, so that it must have a carrying capacity of 4.5 amperes. In order to eliminate, when there is no specimen in the apparatus, any deflection of the moving coil due to the magnetizing effect

which the main solenoid exerts on the yokes, compensating turns C C are wound about the yokes near the test coil and connected in series with the main solenoid, but in such a direction that they oppose the main magnetomotive force. The effective value of the current in the compensating turns is adjusted by shunting until there is no deflection of the coil when the maximum current is flowing but with no test specimen in place.

Through the coil *h* is maintained a current of such a value that the deflection due to the reaction between the coil and the field, as read on the uniform scale, is numerically equal to the flux density in the specimen.

This current is inversely proportional to the cross section of the specimen and is equal to a constant divided by the cross section.

All the newer apparatus is adjusted by the maker until this constant is 0.005. The standard rod 0.6 cm in diameter therefore requires an auxiliary current of 0.2827 ampere.

In the use of the instrument it is necessary to observe several precautions. The instrument should be so oriented that the axis of the moving coil is in the plane of the magnetic meridian; otherwise, there will be a small torque due to the magnetic field of the earth. Masses of iron, particularly if magnetized as in the case of many electrical instruments, should be removed from the immediate neighborhood of the apparatus. The specimen should be of such length that it will not project any considerable distance beyond the yokes. Projecting ends may modify the field in the place occupied by the moving coil. Care should be taken that the glass cover does not collect a charge of static electricity. Such charges may exert a force on the light aluminium pointer sufficient to introduce an error in the induction. After inserting the test specimen in the apparatus it should be thoroughly demagnetized. Residual induction in the bar or yokes will cause a deflection of the instrument even when no magnetizing current is flowing. It is very difficult to reduce this residual deflection to zero, but it should be made quite small, not over a few hundred gauss. To eliminate the errors due to residual induction in the yokes, to a displacement of the zero point, or to the earth's field (since this has an effective component when the coil is in the



FIG. 2.—*Photograph of the Koepsel permeameter used in this investigation*

deflected position) it is necessary to take readings on both sides of the zero point. This may be done by reversing either the auxiliary or the magnetizing current, preferably the latter, since in that method partial correction is made for errors due to the imperfect demagnetization of the test piece.

In the present investigation the normal induction data were obtained by reading the magnetic inductions with the magnetizing current first in one direction and then in the reverse direction. The mean of these two readings gives more consistent results than the method, given in the maker's instructions, of varying the magnetizing current step by step without reversals. In determining the hysteresis data, however, the step-by-step method was followed.

3. CONSISTENCY ON REPETITION

The first requirement of a permeameter is that it shall give the same readings on different determinations of the same material. Table 1 shows two sets of data taken in succession and without removing the test material from the apparatus.

TABLE 1
Typical Koepsel Data
BAR NO. 293, 0.6 CM DIAMETER

H	First set			Second set			ΔB_{mean}
	B+	B-	B_{mean}	B+	B-	B_{mean}	
1	650	25	337	600	100	350	13
2	1700	1100	1400	1650	1150	1400	00
3	3500	2950	3225	3450	3000	3225	00
4	5100	4800	4950	5100	4850	4975	25
6	8000	7900	7950	8000	7975	7987	37
8	10 050	10 000	10 025	10 250	10 000	10 125	100
10	11 500	11 400	11 450	11 500	11 400	11 450	00
20	14 600	14 500	14 550	14 700	14 300	14 500	50
50	16 800	16 400	16 600	16 700	16 450	16 575	25
100	17 950	17 500	17 725	17 900	17 650	17 775	50
300	20 000	19 500	19 750	19 900	19 600	19 750	00
						Mean...	27

B and H are expressed in gaussess. $B+$ and $B-$ correspond to the two directions of the corresponding magnetizing force.

The two readings $B+$ and $B-$ on the two sides of the zero for the same magnetizing force differ widely from each other, especially in the initial inductions. These differences are probably due to a residual induction of the yokes, although very great care was used in demagnetizing. This failure to get complete demagnetization of the yokes is due to the fact that in some earlier use of the apparatus with test rods of larger diameter the yokes were carried to a higher flux density than can be reached with the smaller rods. Other experiments have shown that a closer equality between the two readings is obtained when care has been taken to demagnetize the yokes with a large rod in place before the smaller one to be tested is inserted.

The individual readings in the two sets of data given above differ quite appreciably, but the mean values of each set differ only slightly. Experiment shows that if more careful demagnetization of the yokes had been carried out, as indicated above, the resulting mean values would have been in substantial agreement with those here obtained. The differences noted in the last column of Table 1 may all be accounted for as errors of observation. The smallest graduation on the scale is about 2.5 mm long and represents an induction of 500. The maximum difference in the table of 100 gaussses represents an error of one-fifth of a division and may be distributed over four readings. The mean difference of 27 corresponds to an error in estimation of $1/18$ division. We may conclude, therefore, that this apparatus yields results which are reproducible.

4. SHEARING CURVES

To test the accuracy of the data obtained by the Koepsel apparatus a number of rods were measured by this apparatus, and also by the author's compensated double-yoke method.*

Fig. 3 may be taken as representing the results of such a comparison. The Koepsel apparatus indicates a magnetizing force which is too high for the lower inductions. This error in magnetizing force increases as the induction increases up to a certain stage, when it decreases, passes through zero, and reaches a maximum of opposite sign. Finally it approaches the zero value again and in some cases even changes sign a second time.

* Burrows: "The determination of magnetic induction in straight bars." *This Bulletin*, 6, pp. 31-33; 1909 (Reprint No. 117).

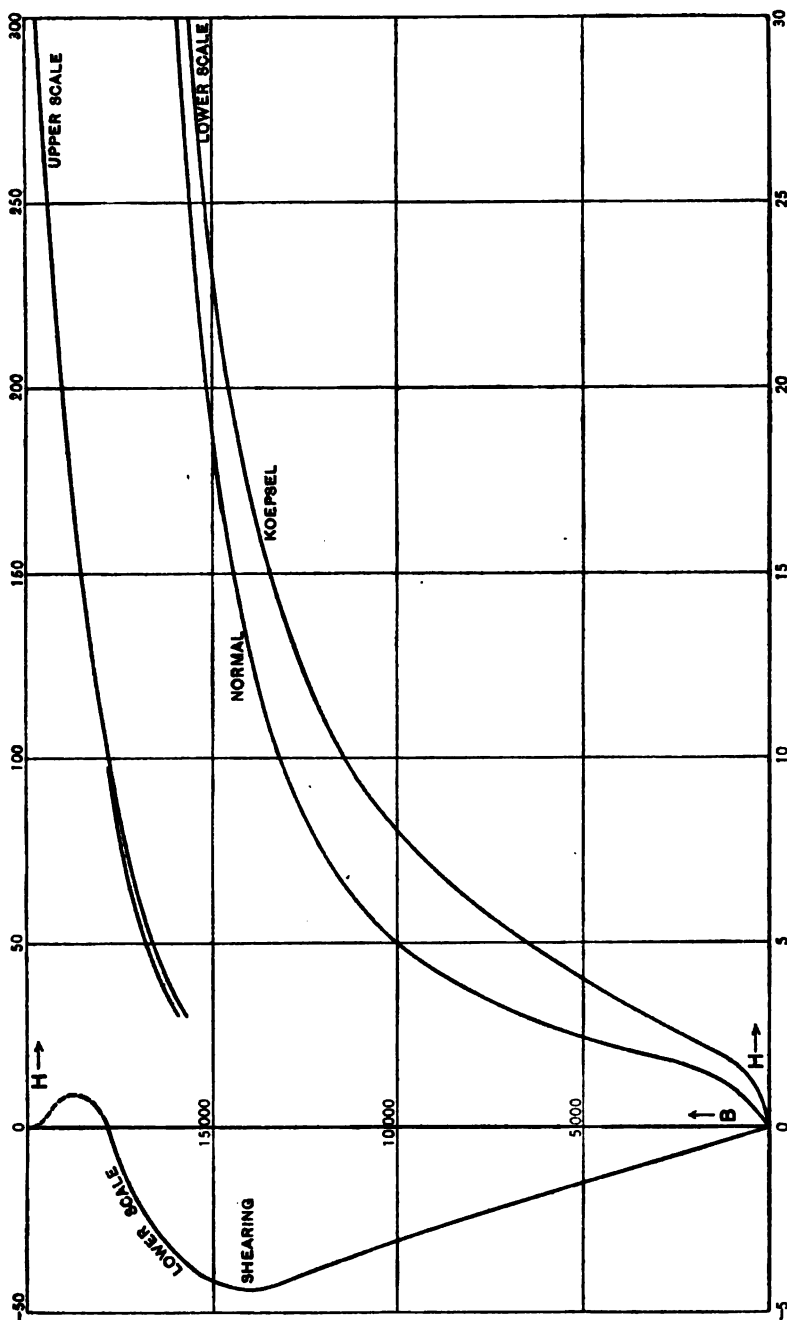


FIG. 3.—Showing the normal induction and shearing curves of a wrought iron rod 0.6 cm in diameter as measured by a Koepsel permeameter

These variations are well shown in the curve of corrections or "shearing curve," as it is usually called. The true points on the induction curve are obtained from the observed values by a shearing parallel to the H axis by an amount equal to the abscissa of the point on the shearing curve having the corresponding induction.

If the shearing curve is constant for specimens of different size and quality, the apparatus would be perfectly reliable for permeability measurements. Unfortunately, however, this correction is not a constant nor does it vary according to any simple law. Figs. 4, 5, and 6 show the normal induction and shearing curves for wrought iron, low-carbon steel, and high-carbon steel, as obtained on the Koepsel apparatus. For comparison, the shearing curves are brought together in Fig. 6. This set of curves shows a number of interesting things. At an induction of 5000 gauss the correction to be applied to the observed magnetizing force is negative and increases in magnitude as we pass from wrought iron to low-carbon steel and to high-carbon steel; that is, the shearing correction is greater for the harder material. At an induction of 15 000 gauss each correction curve has crossed both of the others and the order is completely reversed. The curves show zero correction at inductions which increase as we pass from the hard to the soft material. The maximum positive correction and the maximum negative correction occur at inductions which are lower for the hard material than for the softer material.

It is obvious that the correction does not depend on the induction alone. For accurate use the apparatus should be accompanied by shearing curves of material similar to that under examination. The result of using a shearing curve determined from material which is slightly different from the test material is shown in Table 2. The shearing curve used is that of a low-carbon steel while the test material is wrought iron. The full normal and shearing curves of these two rods are shown in Fig. 6. Table 2 shows that the use of the low-carbon shearing curve results in an error of 10 per cent or over in magnetizing force. If shearing curves of substantially the same material as the test specimen are used, data correct within 5 per cent may be expected.

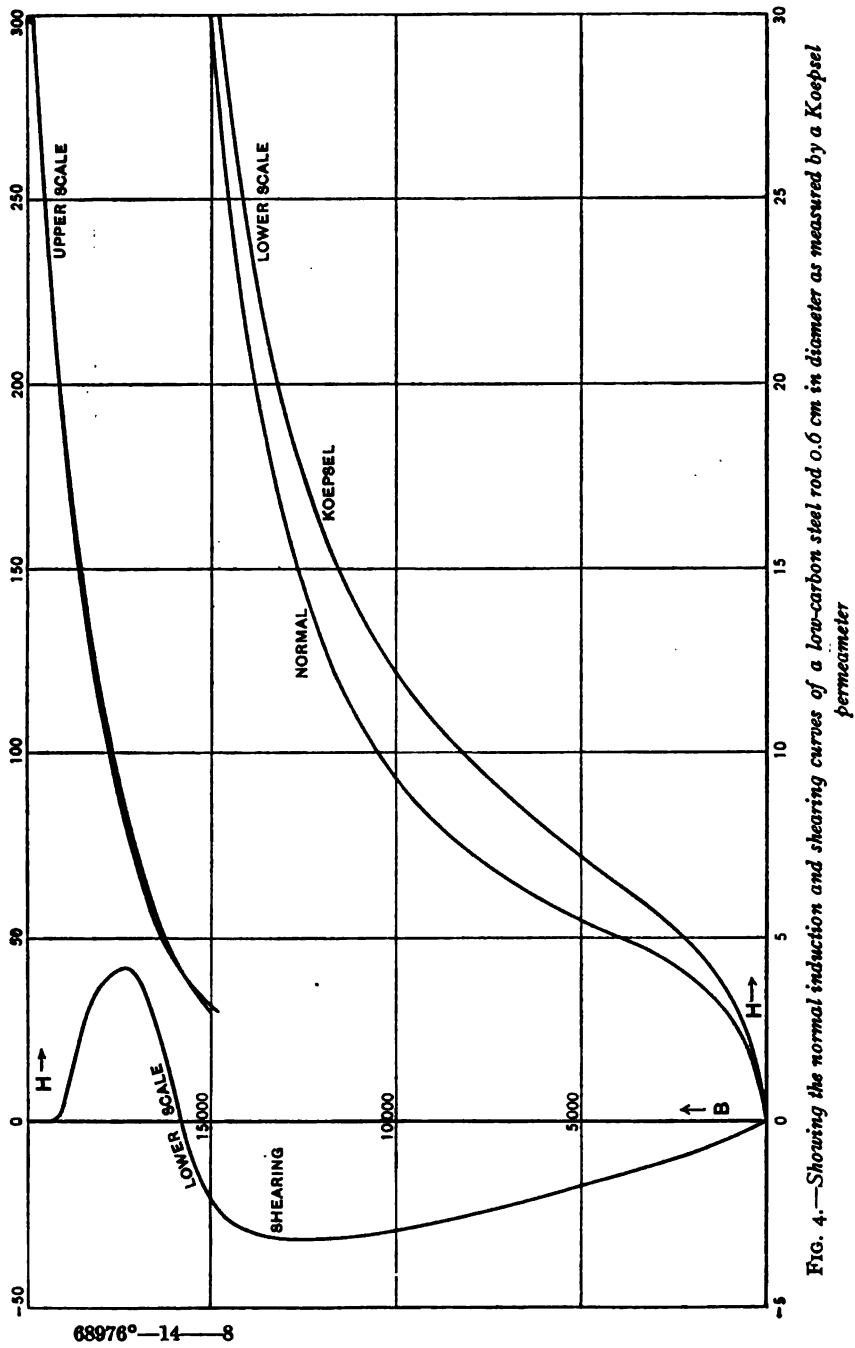


FIG. 4.—Showing the normal induction and shearing curves of a low-carbon steel rod 0.6 cm in diameter as measured by a Koepsel permeameter

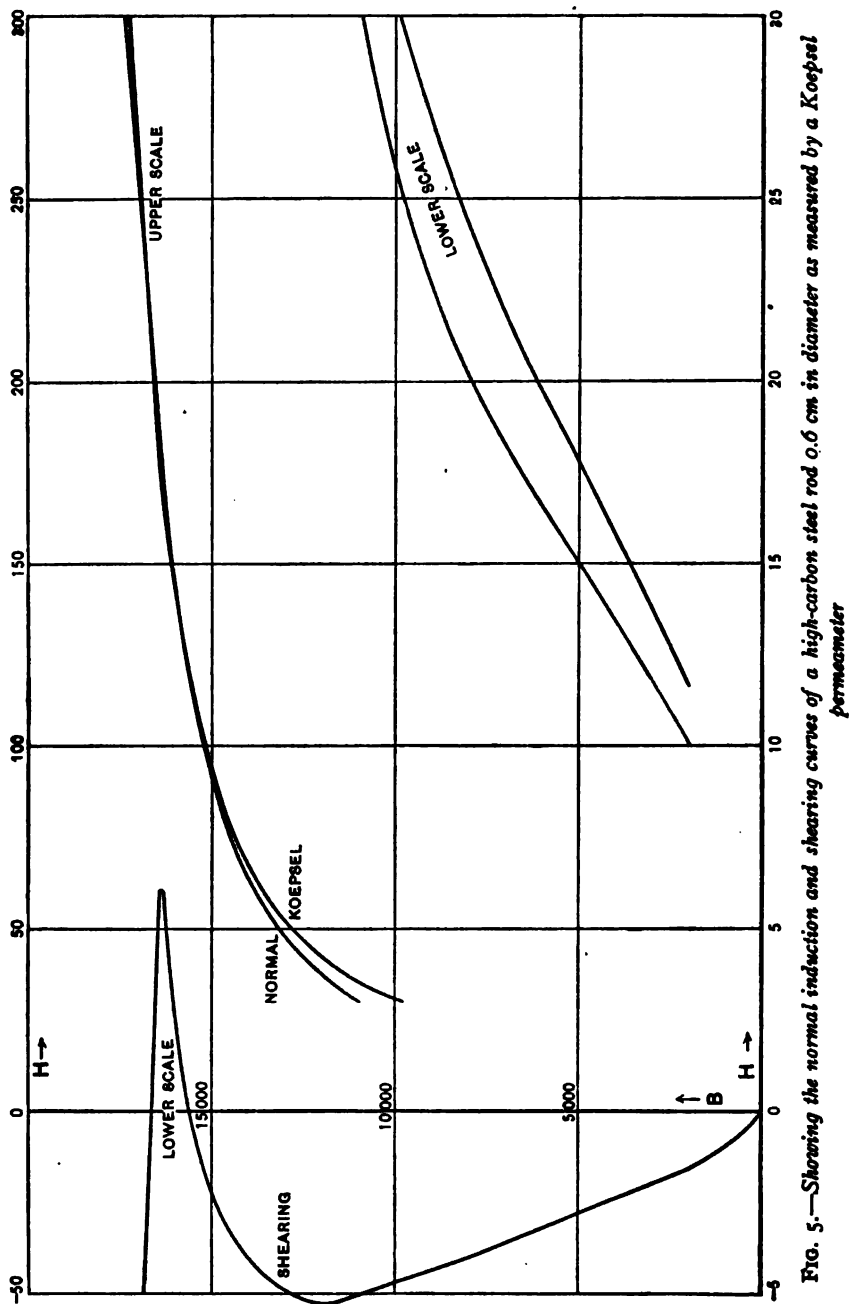


FIG. 5.—Showing the normal induction and shearing curves of a high-carbon steel rod 0.6 cm in diameter as measured by a Koepsel permeameter

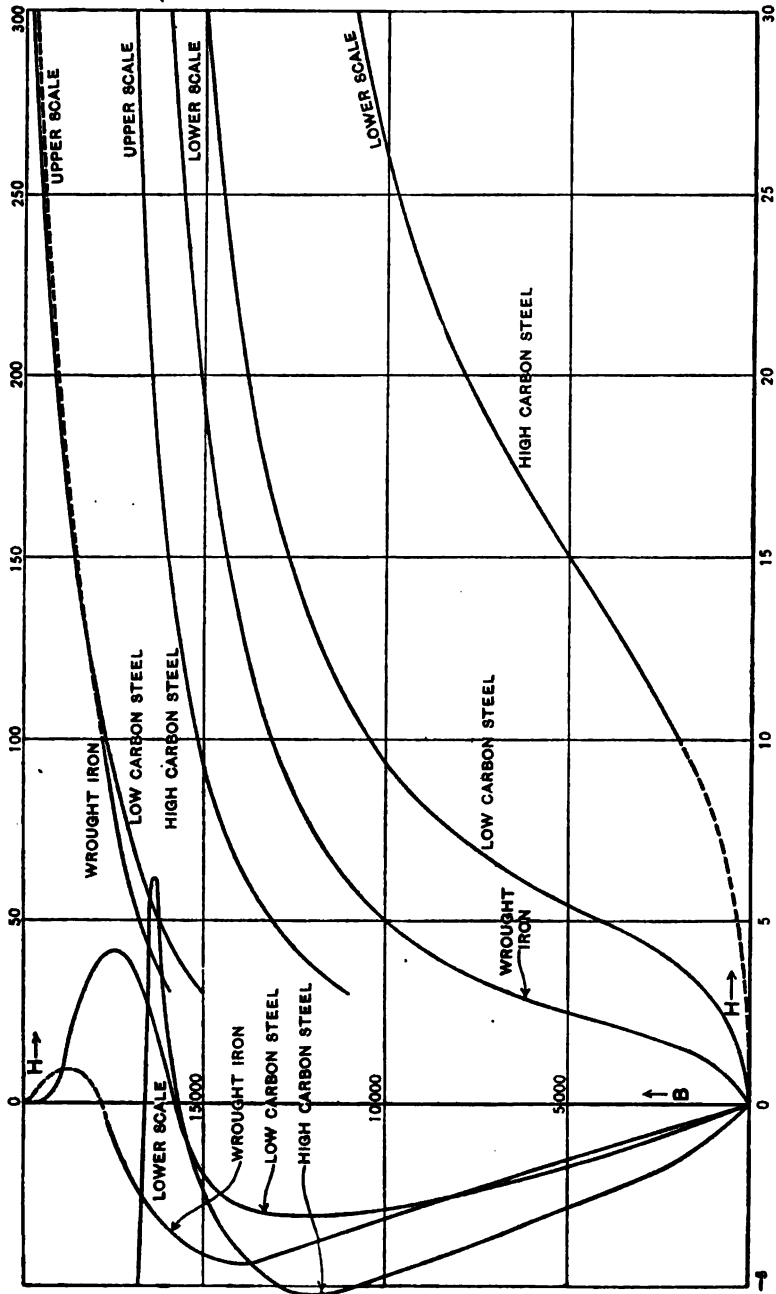


FIG. 6.—Showing normal data and the variation of the Koepsel shearing curve with different materials

TABLE 2

Showing the Results of Using a Low-Carbon Steel Shearing Curve with Data
Obtained on Wrought Iron

B gausscs	H true gausscs	H (wrought iron) - H (steel)	Shearing applied	Error in H	Percent error in H
2 000	1.60	- 2.30	-0.78	-0.16	-10
4 000	2.20	- 2.85	-1.45	-0.25	-11
6 000	2.84	- 3.15	-2.02	-0.20	- 9
8 000	3.68	- 3.65	-2.50	-0.04	- 1
10 000	4.98	- 4.35	-2.90	+ .26	+ 5
12 000	7.35	- 5.65	-3.10	+ .76	+12
14 000	12.95	- 7.9	-2.86	+1.50	+12
16 000	30.00	-15.1	+1.00	+4.45	+15
18 000	115.00	.0	+3.70	+3.2	+ 3

5. CROSS SECTION OF SPECIMEN

The influence of cross section was determined by using narrow strips and building them up into bundles of different cross sections. These strips were cut from the same material and a preliminary examination was made to make certain that the individual strips were substantially equivalent magnetically. Fig. 7 shows the curves for strips of transformer steel (silicon steel) 0.037 cm thick. This material was tested in bundles of 4, 8, and 16 strips. The curves all intersect at approximately 10 000 gausscs. For all points below this intersection the apparent magnetizing force is greater for the bundles of greater cross section. For all points above this intersection the reverse is true and in more marked degree. For instance, at an induction of 16 000 gausscs the observed magnetizing forces for the 16, 8, and 4 strips are 52, 95, and 285 gausscs, respectively.

Similar experiments were performed on a low-carbon steel, using, in this case, rectangular rods 0.39 by 0.63 cm in cross section. The curves in Fig. 8 show the same general characteristics. They intersect at an induction of 13 000 gausscs, and below this value the two rods in parallel require a larger apparent magnetizing force than one alone. The two rods were tested separately and showed quite appreciable differences. The curve has been plotted from the mean values of the two separate rods.

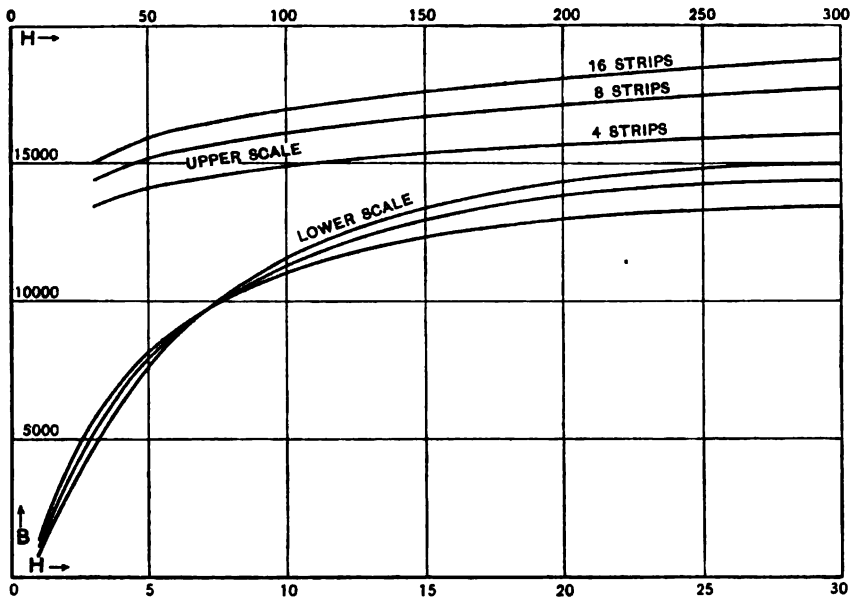


FIG. 7.—Showing the variation of Koepsel data of transformer steel for differences in cross section

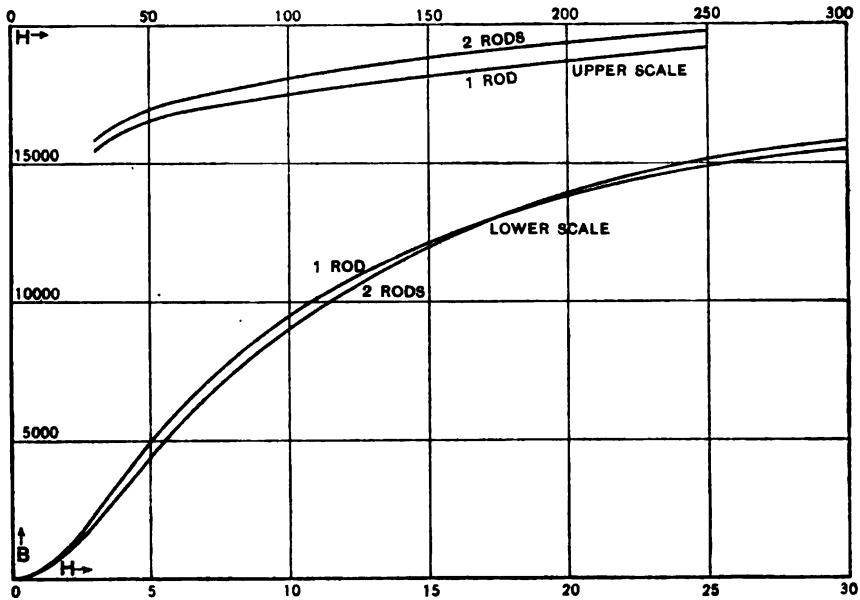


FIG. 8.—Showing the variation of Koepsel data of low-carbon steel for differences in cross section

The changes in cross section were quite large in the cases of the wrought iron and low-carbon steel, and the question arises whether small variations in cross section are proportionately important. To test this point and also to get data on a harder material 11 strips of tempered steel tape 0.63 cm wide and 0.047 cm thick were measured in groups of 8, 9, 10, and 11 strips. Fig. 9 shows the extreme curves for the greatest and least cross sections. The other curves are not shown in the figure but lie between those shown here. These curves show the same characteristics in the

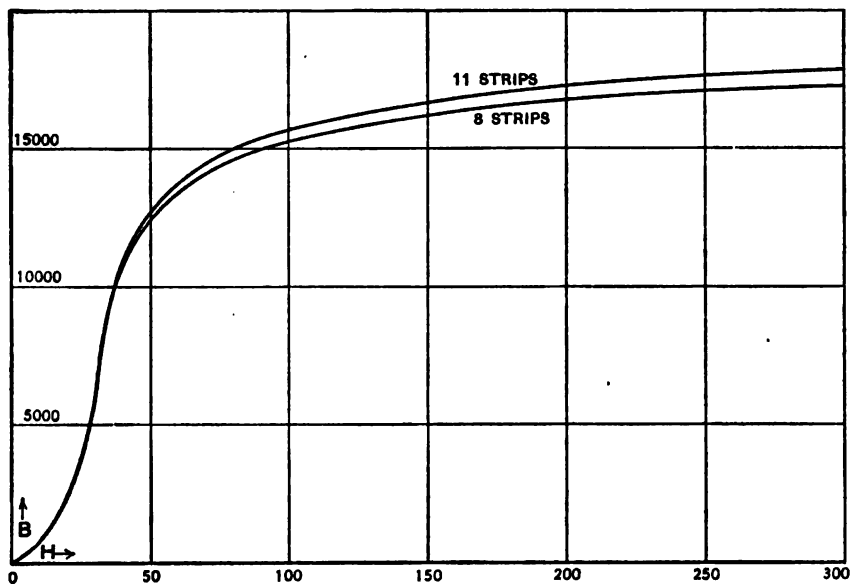


FIG. 9—Showing the variation of Koepsel data of tempered spring steel for differences in cross section

upper portions as the preceding. The point of crossing, which is so conspicuous with the softer material and the greater range of cross sections, is barely discernible in the numerical data but would probably develop if a greater range of cross sections had been tried.

From the preceding it is quite evident that separate shearing curves must be supplied, not only for test samples of different materials, but also for test samples of the same material which have widely different cross sections.

6. LENGTH OF SPECIMEN

It seemed quite probable that the length of the specimen might have some influence on the reading of the instrument. With a view of determining the magnitude of any such influence the following experiment was made. A rod 123 cm long was inserted in the Koepsel apparatus with equal lengths projecting beyond each yoke, and measurements taken. The rod was then removed and 10 cm cut off from each end. Magnetic measure-

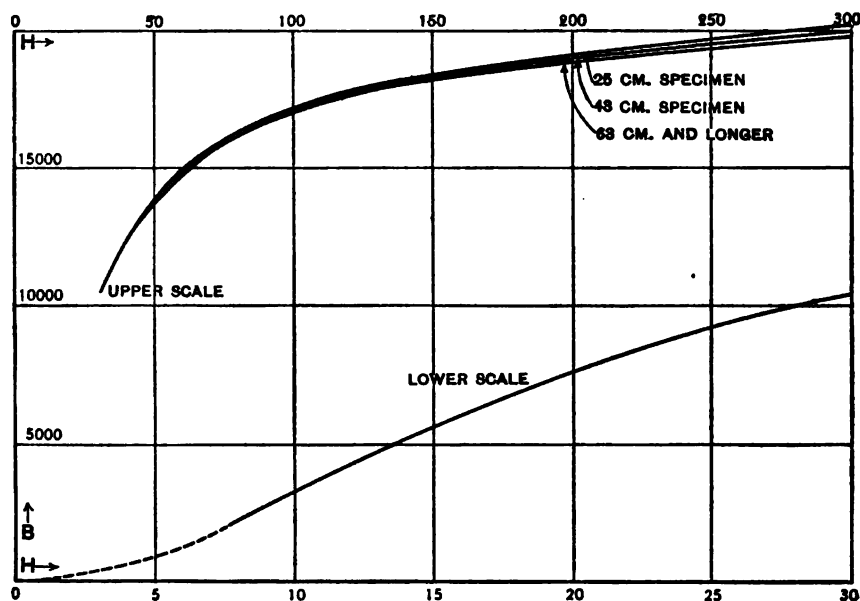


FIG. 10.—Showing the effect of using specimens whose ends project beyond the yokes of the Koepsel apparatus

ments were taken as before, taking care that the same portion of the rod was within the apparatus. This operation was repeated until the rod had been reduced to the minimum length that could be used in the apparatus. No change in the readings was noticed until the length of the specimen was reduced below 63 cm.

Fig. 10 shows the curves for lengths of 25, 43, and 63 cm. No variation is noticed in points below the knee of the curve. At higher inductions the curves diverge more and more as the induction increases. The shorter specimens require a lower magnetizing

force. The difference is so slight that projections of several centimeters are not serious.

7. POSITION OF BUSHINGS

A more serious source of error is in the proper placing of the bushings. In one run the bushings were inadvertently left pro-

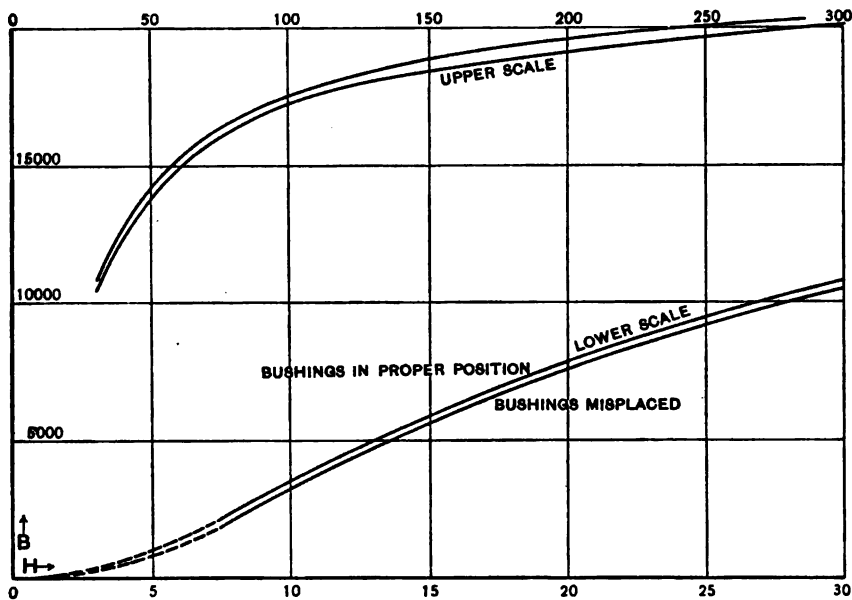


FIG. 11.—Showing the effect of improper placing of the bushings in the Koepsel apparatus

jecting beyond the yokes on the outer side by about 5 mm. This has the effect of increasing the effective length of the portion of the specimen tested. Fig. 11 shows the two curves obtained with the bushings misplaced as indicated and with the bushings flush with the yokes as they should be. The differences indicate that some care should be exercised in inserting the test specimen in the apparatus.

8. FLUX DISTRIBUTION IN THE KOEPEL APPARATUS

The preceding experimental results show that the correction to be applied to the readings with the Koepsel permeameter, to reduce them to true values, depends upon several factors. It has been shown that the magnitude of this correction depends upon the material, length, and cross section of the specimen under test, and also the magnetic condition of the yokes and the position of the bushings.

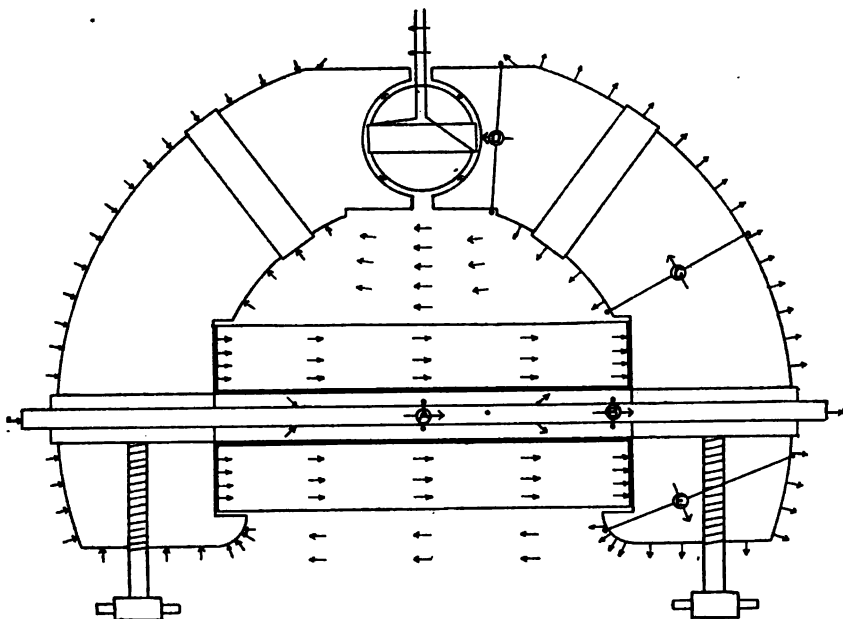


FIG. 12.—Showing the location of the exploring coils used in the determination of the flux distribution, and the approximate direction of the magnetic flux

In order to determine more fully the nature of the influence which each of the conditions exerts on the resultant observed values of magnetizing force and magnetic induction, it seems desirable to determine the flux distribution along different parts of the magnetic circuit.

We know that in a general way the magnetic flux in an apparatus of this type is distributed somewhat as shown by the arrows of Fig. 12.

To secure quantitative results on the flux distribution, exploring

coils of 10 turns each were wound around different cross sections of the magnetic circuit. These were placed over the portions indicated in Fig. 12, by the letters A, B, C, D, and E. Full magnetization curves were taken both with and without current in the compensation coils. A condensed view of the results is given in Tables 3 and 4, where the various fluxes are expressed in terms of the flux through the coil surrounding the center of the test

TABLE 3

Showing the Relative Distribution of the Flux in the Koepsel Apparatus with Normal Compensation. (See Fig. 12)

Current	A	B	C	D	E	C+E	A-B	Decrease in A, due to com- pensation
Amperes								
0.15	1.00	0.93	0.86	0.76	0.07	0.93	0.07	0.03
0.30	1.00	0.93	0.87	0.78	0.06	0.93	0.07	0.01
0.60	1.00	0.93	0.88	0.79	0.06	0.94	0.07	0.01
3.00	1.00	0.95	0.94	0.79	0.11	1.05	0.05	0.00

TABLE 4

Showing the Relative Distribution of Flux in the Koepsel Apparatus Without the Compensation. (See Fig. 12)

Current (amperes)	A	B	C	D	E	A-B	C+E
0.15	1.00	0.93	0.88	0.79	0.06	0.07	0.94
0.30	1.00	0.93	0.90	0.81	0.05	0.07	0.95
0.60	1.00	0.95	0.92	0.83	0.05	0.07	0.97
2.00	1.00	0.95	1.00	0.91	0.05	0.05	1.05
3.00	1.00	0.95	1.05	0.95	0.05	0.05	1.10

rod. The test rod itself is a low-carbon steel rod of rectangular section 0.9 cm square. The difference, A-B, represents the magnetic leakage from the bar between the center and either end; that is, between A and B. This leakage is nearly constant, but is slightly lower for the higher inductions. It is practically the same with as without the compensation. This leakage flux gives rise to magnetic poles. Due to these poles there is a magnetic force acting in the space occupied by the middle portion of the test rod. This is a demagnetizing force, which varies with the

pole strength or, what is proportional to it, the leakage. We see, therefore, that this self-demagnetizing effect is proportional to the magnetic induction, except for points near saturation, where it is somewhat below proportionality. It is what is left of the much larger self-demagnetizing force that would exist if the ends of the bar were not connected by yokes.

The sum $C + E$ is a measure of the greater portion of the flux that enters the yoke. It does not measure the whole flux which enters the yoke, since only those portions which leave through sections C and E are included. The yoke between these two sections is the seat of some leakage, which has been neglected. This flux $C + E$ is less than the flux through the specimen for the lower inductions, but becomes greater as saturation approaches. This latter condition means that more flux enters the yokes than leaves the bar. The resulting polarity of the yokes is the seat of a positive magnetizing force. It is less with the compensation than without it. The explanation of this extra flux is considered more fully in the next section.

The flux through E is the return flux which passes between the yokes through the air without linking the moving coil. It increases at the higher inductions when the compensation is used, but decreases when it is not used.

Column D is the ratio of the flux through the moving coil to the flux through the center of the test rod. If this ratio and the relative leakage around the poletips are constant, the flux through the test coil may be used as a measure of the flux in the specimen. However, this ratio is not constant. Without compensation, it varies from 79 per cent to 95 per cent of the flux through the test piece. With compensation, the ratio is more nearly constant, showing a flux of from 76 per cent to 79 per cent of the flux through the test piece. The variation of this ratio is, therefore, about 2 per cent of its own mean value.

If the scale is calibrated so that the magnetic induction read is proportional to the deflection of the moving coil, the scale may be so calibrated that the induction readings at any point on the scale are not in error by over 1 per cent. This variation at an induction of 20 000 gaussses corresponds to an error in the corresponding magnetizing force of 5 per cent or more.

9. THE DIRECT MAGNETIZATION OF THE YOKES BY THE SOLENOID

The excess of flux in the yokes over that in the bar is due to the magnetizing force which is exerted on the yokes by the magnetizing solenoid. The total mmf acting along the yokes of the magnetic circuit is no inconsiderable portion of the applied mmf.

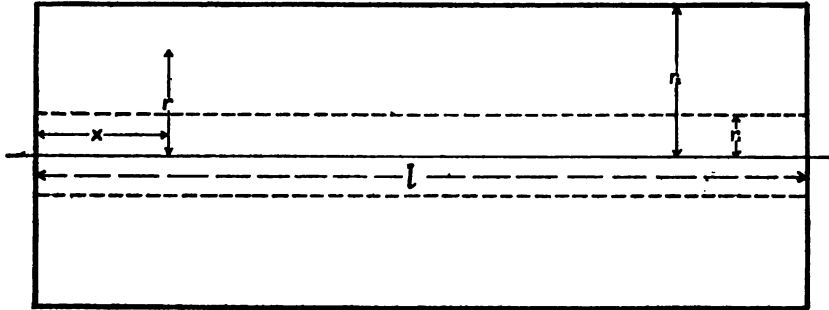


FIG. 13.—Representing a solenoid of length l whose inner and outer layers have the radii r_1 and r_2 respectively

If r = radius of any layer

x = distance of a point on the axis from one end of the solenoid

I = current in amperes

n = number of turns per cm

H = magnetizing force in gausses

Then

$$H = \int_{l-x}^x \frac{0.2\pi r^2 n I dx}{(r^2 + x^2)^{3/2}}$$

$$= 0.2\pi n I \left\{ \frac{x}{\sqrt{r^2 + x^2}} + \frac{l-x}{\sqrt{r^2 + (l-x)^2}} \right\}$$

This equation gives the magnetizing force for any point on the axis of the solenoid.

If now we calculate the magnetomotive force along the axis of the solenoid between the planes bounding its ends, we find for the mmf along that portion of the test bar between the yokes:

$$\int_0^l H dx = \int_0^l 0.2\pi n I \left\{ \frac{x}{\sqrt{r^2 + x^2}} + \frac{l-x}{\sqrt{r^2 + (l-x)^2}} \right\} dx$$

$$= 0.2\pi n I \left\{ \sqrt{r^2 + x^2} - \sqrt{r^2 + (l-x)^2} \right\}_0^l$$

$$= 0.4\pi n I \{ \sqrt{r^2 + l^2} - r \}$$

This last expression is the mmf applied to the bar.

The total mmf of the solenoid is

$$0.4\pi nIl$$

The ratio of the mmf applied to the bar to that of the solenoid is therefore

$$\frac{0.4\pi nI\{\sqrt{r^2+l^2}-r\}}{0.4\pi nIl} = \sqrt{1+\beta^2}-\beta, \text{ where } \beta = \frac{r}{l}$$

$$= 1 + \frac{\beta^2}{2} - \frac{\beta^4}{8} +, \text{ etc.}$$

The proportion of the total mmf applied to the yokes is the difference between the above quantity and unity; that is,

$$\beta - \frac{\beta^2}{2} + \frac{\beta^4}{8} - \text{etc.} \quad \text{eq. (1)}$$

In the case of the solenoid of the Koepsel apparatus

$$\begin{aligned} r_1 &= 0.85 \\ r_2 &= 2.70 \\ r_{\text{mean}} &= 1.78 \\ l &= 12.7 \\ \beta &= \frac{1.78}{12.7} = 0.14 \end{aligned}$$

Substituting $\beta = 0.14$ in equation (1)

$$\begin{aligned} \text{we have } \beta - \frac{\beta^2}{2} + \frac{\beta^4}{8} &= 0.14 - \frac{0.14^2}{2} + \frac{0.14^4}{8} \\ &= 0.140 - .010 + .000 \\ &= 0.13 \end{aligned}$$

that is 13 per cent of the total mmf of the solenoid is applied directly to the yokes.

This result is calculated on the assumption that the portion of the mmf applied to the yokes is the same as if the coil were concentrated in one layer at its mean radius.

10. THE MAGNETIZING FORCE

The magnetizing force acting on the center of the bar is the resultant of at least five components.

The most important is the magnetizing solenoid itself. This is the only one that can be calculated directly and it is very desirable to construct the apparatus so that all the other components of

magnetizing force neutralize each other. The next best condition is to have these secondary magnetizing forces directly proportional to that exerted by the main solenoid. In the present piece of apparatus neither of these conditions is fulfilled.

The compensating coil C, Fig. 1, contributes a small demagnetizing force at the center of the bar. This is shown in the last column of Table 3 by indicating a lower actual induction in the bar when the compensation is used than when no compensation is used. This difference produces a change in induction as great as 3 per cent at low intensities and vanishes at the higher inductions. This demagnetizing force is small and may be considered as approximately 3 per cent of the total magnetizing force at the lower inductions, and is negligible at the upper values.

The magnetic field of the solenoid acts on the yokes in such a direction as to produce a positive magnetizing force in the space occupied by the test bar. This magnetizing force is proportional to the current and consequently, if plotted as abscissæ against induction as ordinates, would give a curve of the same shape as the normal B—H curve. This reactive force of the yokes has been noted before in other forms of magnetic circuit.¹⁰

The bar itself presents magnetic poles which exert a magnetizing force both on the bar and on the yokes. This magnetizing force opposes that due to the solenoid as far as the rod is concerned. It is this demagnetizing force which plays so important a part in straight bars with air-return magnetic circuits.

This magnetizing force acts also on the yokes, thus producing a positive magnetizing force in the region occupied by the bars. Each of these effects is proportional to the leakage from the bar, and if the resultant poles were fixed in position they might be considered as a single influence. However, the distance between the poles is a function of the permeability of the bar and increases as the permeability decreases. Consequently, we might expect the demagnetizing effect of the poles to predominate at the lower inductions where the permeability is high and the corresponding magnetizing effect of the yokes to predominate at the higher inductions where the permeability of the specimen is low. These

¹⁰ Burrows: "The determination of magnetic induction in straight bars," this Bulletin, 6, p. 45; 1909 (Reprint No. 117).

effects would be accentuated in test specimens of larger cross section, in which the leakage is greater in magnitude, thus exerting a greater field in both the bar and the yoke.

11. FLUX DENSITY

In the Koepsel apparatus the flux density through the center of the test bar is measured in terms of the field in the gap in which the test coil swings. This field is influenced by the magnitude of the flux in the test specimen, the flux in the yokes due to the magnetizing force of the solenoid, the flux due to the compensating turns, the flux due to the current in the moving coil, and also the various leakage fluxes.

The flux through the center of the test specimen is the quantity we wish to measure, and it is desirable that this flux have a constant ratio to the field in the gap in which the coil swings. If this is true, then the instrument may be calibrated so as to read true flux densities in the bar. To do this all the other flux components must add up to zero or give a resultant which is proportional to the flux in the bar. That neither of these conditions is fulfilled is seen from the data of Table 2. The total flux through the gap is always less than the flux through the specimen, but the difference becomes relatively less as the induction increases. Accordingly, if the instrument is calibrated at low or moderate inductions the higher inductions would give a reading too high or, what is equivalent, the corresponding correction to the observed magnetizing force would become positive.

The flux due to the magnetization of the yokes by the main magnetizing solenoid is nearly proportional to the current, since the iron of the yokes is worked at comparatively low inductions. The corresponding component of the shearing curve has the shape of a normal induction curve and becomes important only at the higher inductions.

The effect of the compensating turns is to reduce the flux caught by the moving coil. This effect is nearly proportional to the current and, consequently, greater at the higher inductions. It likewise contributes to the shearing curve a component which has the same shape as a normal induction curve.

The leakage flux between the ends of the specimen is very considerable, but combines with that due to the compensating turns to produce a nearly constant ratio of leakage, as shown above.

The magnetomotive force of the moving coil is relatively small. This coil has 30 turns which, for a normal specimen, corresponds to a magnetomotive force of 11 cgs units. The total magnetomotive force of the solenoid is about 12 *H* cgs units. The magnetomotive force of the test coil has only a small component along the direction of the main magnetic flux. However, it is concentrated at the most effective part of the circuit and undoubtedly exerts an appreciable influence.

Another element which is a source of error in the measurement of the flux density is the determination of the constant of the instrument. An error in the determination of this constant or in the setting of the auxiliary current introduces a proportional error in the measurement of the induction. The corresponding error in the magnetizing force depends upon the relative rate of change of the magnetizing force necessary to produce this change in induction. Table 5 contains a set of normal data and the changes in magnetizing force which correspond to 1 per cent change in induction. From this table we see that a change of 1 per cent in the induction corresponds to changes in magnetizing force varying from 0.4 per cent at the maximum permeability to 9 per cent at 20 000 gauss.

TABLE 5

Showing the Percentage Variations in *H* Corresponding to 1 Per Cent Variation in *B* for Low-Carbon Steel

<i>B</i> gauss	<i>H</i> gauss	$\frac{H}{B} \times 1000$	$\frac{H}{B} \times \frac{B}{100}$	Percentage variation in <i>H</i>
2000	3.89	0.74	0.0148	0.38
4000	4.93	.45	.0180	.36
6000	5.96	.48	.0288	.47
8000	7.28	.77	.0616	.85
10 000	9.30	1.25	.125	1.35
12 000	13.01	2.66	.319	2.46
14 000	21.36	7.25	1.07	5.01
16 000	44.18	17.5	2.80	6.35
18 000	116.3	52.	9.36	8.1
20 000	314.3	145.	29.0	9.2

12. HYSTERESIS DATA ON THE KOEPEL PERMEAMETER

The Koepsel permeameter may be used for the determination of the hysteresis loop as well as for the measurement of permeability. Fig. 14 shows a set of data as obtained on this appa-

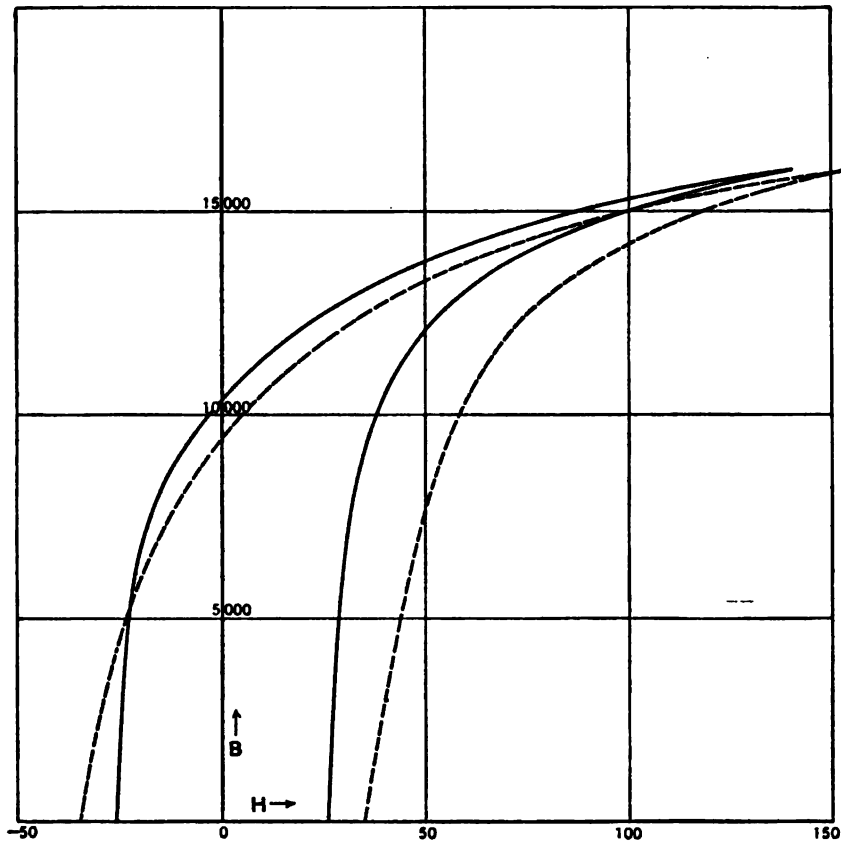


FIG. 14.—Showing one half of a typical hysteresis loop for unhardened magnet steel as obtained by the author's method (solid line) and as obtained by the Koepsel permeameter (broken line)

ratus, together with that obtained by the author's method. These data are for an unhardened magnet steel, but show characteristics that are found in all hysteresis determinations.

As we saw in the permeability measurements the magnetizing force corresponding to the tip of the loop is too high for the

Koepsel. The residual induction is lower and the coercive force is higher as obtained by this apparatus. The two curves intersect between the points represented by the residual induction and the coercive force.

The relation between the magnetizing forces at the tips of the curves, as obtained by the two methods, depends upon the nature of the material investigated and upon the maximum induction

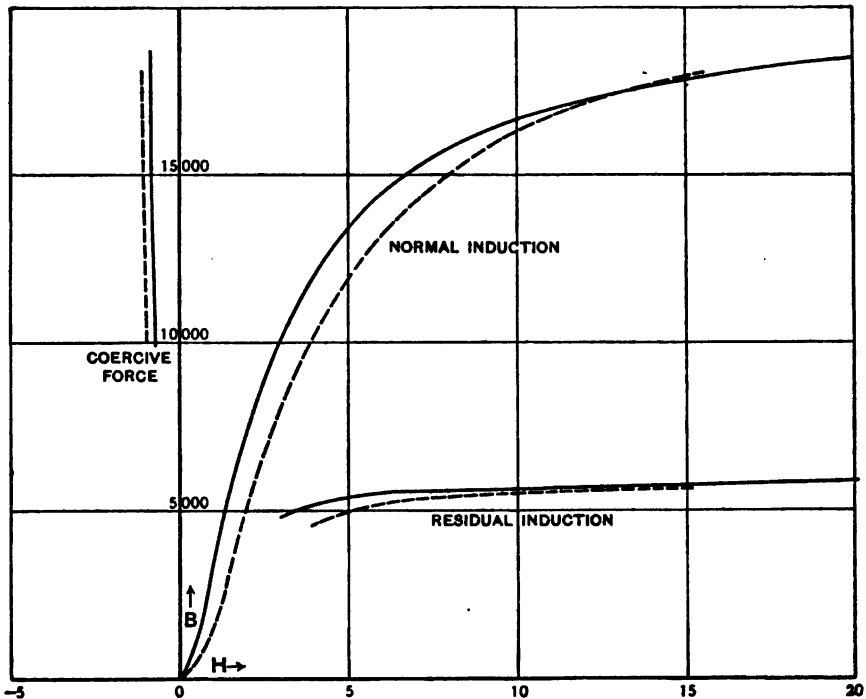


FIG. 15.—Showing curves of normal induction, residual induction, and coercive force for a sample of low-carbon Bessemer steel as obtained by the author's method (solid line) and by the Koepsel method (broken line)

obtained. The other characteristics are the same qualitatively for all loops of any material. Different materials differ only in degree.

On Fig. 15 are plotted the curves of maximum induction against magnetizing force, of residual induction against magnetizing force, and of coercive force against normal induction for various hysteresis loops taken with the same specimen. It is to be noticed here that the observed curve representing the tips of the loops

crosses the true curve at a moderately high value. The observed residual induction curve is always lower than the true curve. The observed coercive force curve shows values of the coercive force always too large, no matter what maximum induction is used.

Figs. 16 and 17 show similar data for harder materials. From a comparison of the three figures it is evident that the residual induction as obtained on the Koepsel apparatus is always too

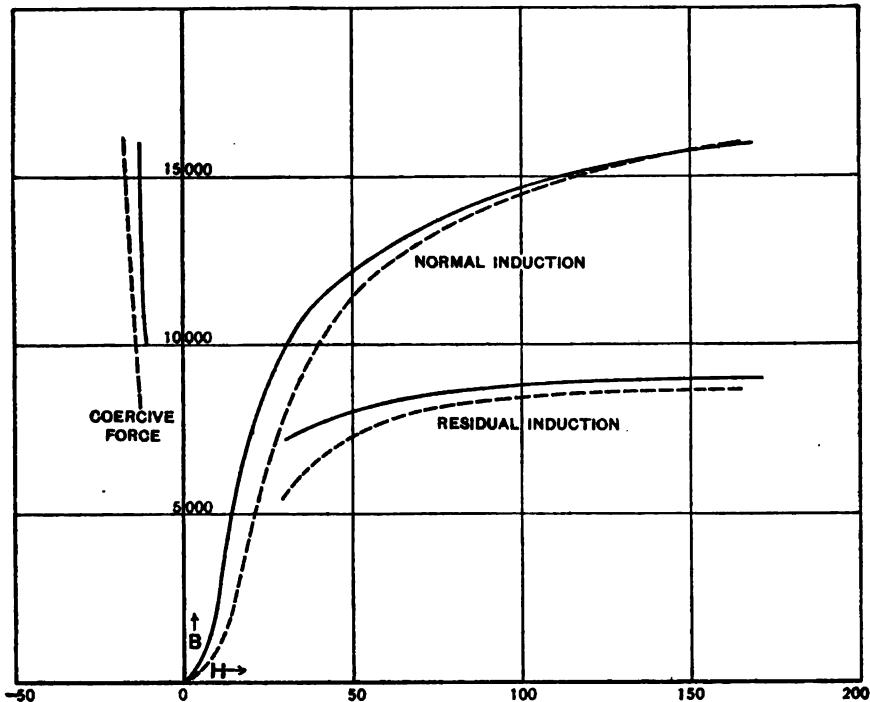


FIG. 16.—Showing curves of normal induction, residual induction, and coercive force for a sample of tool steel as obtained by the author's method (solid line) and by the Koepsel method (broken line)

low and that the error is greater with material having the higher inductions. The observed coercive force which gives too large a value has an increasing error as the coercive force increases.

13. THEORY OF HYSTERESIS ERRORS

The residual induction as measured may be considered as influenced by the residual magnetic fluxes in the bar, yokes, and air gaps. If these three parts of the magnetic circuit had the

same remanence the reading of the instrument which measures the field in the air gap would be proportional to the residual induction in the specimen. However, this is not the case. The air gaps have no remanence, while that of the yokes may be greater or less than that of the test specimen. If it is less than the specimen, it is obvious that the mean remanence is less than that of the specimen alone. If the yokes are of hard material relative

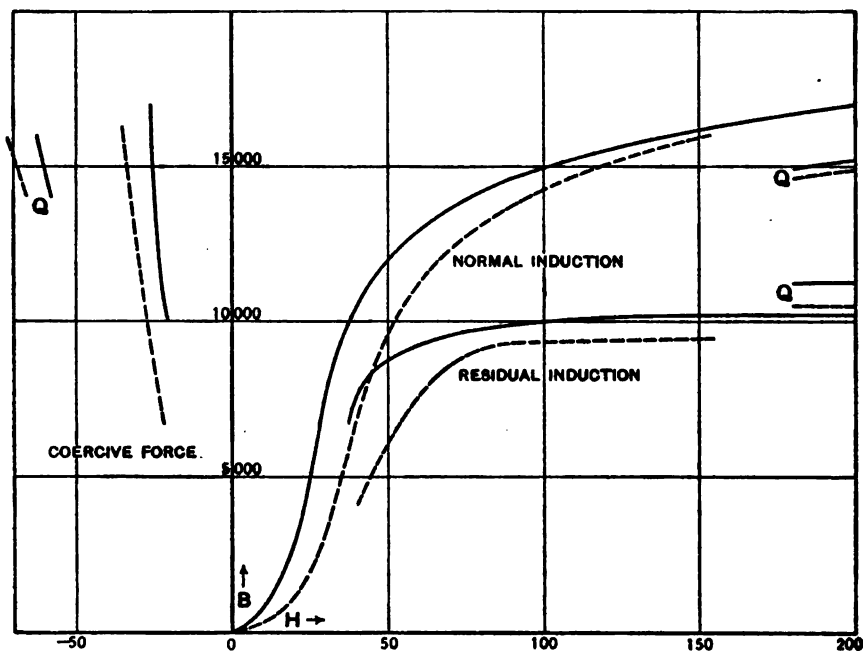


FIG. 17.—Showing the curves of normal induction, residual induction, and coercive force for a sample of unhardened-magnet steel as obtained by the author's method (solid line) and by the Koeppel method (broken line). The short segments *Q* represent similar data on the same material after it has been hardened

to the specimen, they may compensate for the lack of remanence of the air gap and we find the remanence indicated by the moving coil equal to that of the specimen or even greater than it.

The magnetomotive force which is the source of the coercive force is concentrated over the specimen itself, while the condition of no flux in the magnetic circuit is determined at a point somewhat removed from the specimen. The moving coil is in a field

due to the induction in the yokes. After the whole magnetic circuit has been magnetized to a degree represented by the tip of a given hysteresis loop of the specimen and a reversed magnetizing force applied until there is no induction in the test specimen, we still have a residual induction in the yokes. This residual induction of the yokes indicates an incomplete demagnetization of the system, as shown by the pointer attached to the moving coil. To bring this pointer to zero it is necessary to magnetize the test specimen in the opposite direction. The magnetic field then due to the induction in the specimen, acts on the yokes and demagnetizes them. In this condition the instrument reads zero induction, but the test bar is magnetized in the reverse direction under a magnetizing force greater than the true coercive force. The exact nature of the error in coercive force is complicated somewhat by the influence which the magnetizing solenoid and the compensating coil exert on the yokes.

14. CONCLUSION

The Koepsel permeameter has several valuable characteristics. It gives direct readings of the magnetizing force and the magnetic induction, both for normal induction and for hysteresis data. It is easy of manipulation and does not require greater care than the usual deflection instruments. It repeats its readings as consistently as could be desired. The readings may be very useful in indicating relative values of different materials or the degree of nonuniformity of similar materials. The fact that the observed values of the magnetizing force may differ by as much as 100 per cent from the true values does not destroy the value of this instrument for purposes of comparison.

From the experimental consideration of the different factors which may affect the accuracy of the readings the following detailed conclusions were drawn:

1. Readings on the two sides of the zero of the instrument may differ considerably, but the mean of the two values thus obtained shows satisfactory consistency on repetition.
2. Shearing curves for different grades of material show that the correction to be applied to the observed magnetizing force is not constant for a given induction, but depends upon the nature of the test specimen. This correction is usually subtractive for

points below the knee of the induction curve and additive for points above the knee.

3. An increase in the cross section of the test specimen tends to increase the observed values of the magnetizing force for points below the knee of the induction curve, and to decrease the observed values for points above the knee.

4. The length of the specimen projecting beyond the yokes produces no noticeable effect for points below the knee of the induction curve. For points above the knee the projecting ends increase the observed value of the magnetizing force.

5. If the bushings are not pushed all the way into their proper position, a higher apparent value of the magnetizing force is observed, due to the increased length of the portion of the bar under test.

6. Hysteresis loops obtained by the Koepsel permeameter always show a low observed residual induction and a high observed coercive force.

7. A theoretical and experimental study of the distribution of the magnetic fluxes through different parts of the magnetic circuit shows that shearing curves of the form observed are to be expected.

If the apparatus is to be used for the determination of the absolute values of the magnetic quantities, it is necessary to apply a correction to the readings. Since the apparatus gives consistent results on repetition, the whole error may be charged to errors in the correction or shearing curve. As this shearing curve varies with the dimensions and quality of the specimen, it is essential that shearing curves be prepared for each size and quality of specimen to be tested. With extreme care and the use of proper shearing curves, the apparatus is capable of giving quantitative results within 5 per cent of the true value of the magnetizing force for a given induction.

Uncorrected hysteresis data for hard steels show values of the residual induction that are too small; the error may be as great as 10 per cent. Values obtained of the coercive force are systematically too large; the error may be as much as 40 per cent.

WASHINGTON, August 1, 1914.

VARIOUS MODIFICATIONS OF THERMOPILES HAVING A CONTINUOUS ABSORBING SURFACE

By W. W. Coblentz

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I. INTRODUCTION

The linear thermopile, consisting of bismuth and silver wires, with rectangular receivers attached to the junctures of these two metals was constructed about three years ago.¹

Its novelty consists in a series of overlapping receivers, forming a continuous surface which has all the advantages of a good bolometer, with none of the disadvantages of that well-known instrument. At first the wide application of this device could not be foreseen. In fact, the first instrument was constructed in part to refute the prediction that such a design (proposed about a year earlier) was doomed to failure because of lack of insulation. As an illustration of some of the contradictions in mechanical construction it is relevant to say that there is no difficulty in obtaining good insulation, and that one is chiefly concerned in obtaining good metallic contact of the fine wires used in this device.

The object of the present paper is to illustrate various modifications and uses to which this instrument has been adapted, and to indicate further applications.

The wide range of usefulness of this radiometer is owing to the fact that its heat capacity is sufficiently low so that it attains a maximum temperature in less than four seconds (and 92 per cent of its maximum in two seconds); and yet the receiver is sufficiently massive so that it may be operated in the open without being disturbed by the cooling effect of air currents. No doubt the thinnest bolometer material would be more sensitive than the thermopile, when used in a high vacuum, but in that case the general applicability of these two types of instruments is not being considered.

The general utility of the thermopile as a radiometer will be apparent from the various modifications which will be described presently. It will be sufficient to note briefly that the investigation of the effect of radiant energy upon matter, and in passing through matter, and the investigation of the laws governing the passing of energy by radiation from matter, occupies the attention of many of the foremost experimenters. The visible and ultra-violet radiations are being used as stimuli by chemists for producing photochemical reactions, by biologists and physiologists

¹ This Bulletin, 9, p. 7; 1912.

in their investigations of the effect of radiant energy upon lower organisms, by psychologists in their studies of the effect of light upon the eye, and by physicists in their investigations of photo-electric and other phenomena. In all such investigations it is desirable to know the energy value (mechanical equivalent) of the different radiations (wave lengths) used as stimuli. For this purpose it is necessary to use a radiometer which functions independently of the frequency of the stimulus. Many of the aforementioned groups of investigators lack experience in operating a bolometer and have not the time available to acquire such experience even if their laboratories are fortunately so situated as to permit of the use of a bolometer. It is with the needs chiefly of this type of investigators in mind, that the various thermopile experiments herein described have been made.

As mentioned in the first paper ² the selection of silver to complete the element with bismuth was because of the ease with which it can be cleaned (in order to obtain complete contact in soldering the metals) and annealed, which are the prime requisites in construction. It will be shown presently that neatness of construction is of more importance than a high thermal emf in order to produce a thermopile having a high radiation sensitivity.

The present form of bismuth-silver thermopile is the result of experiments upon materials that are sufficiently strong so as to withstand rough usage. In addition to this feature, it has a high sensitivity and a quick action. It is the outcome of an attempt to produce a receiver, having a completely opaque surface (i. e., no open spaces in it), which may be calibrated and used (in air) in making absolute measurements of radiant energy.

II. THEORETICAL DEDUCTIONS OF EFFICIENCY OF THERMOPILES

In connection with the question of the possibility of replacing the dynamo by a thermoelectric generator, Rayleigh ³ has discussed the thermodynamic efficiency of the thermopile. In his computations only the specific resistances and the thermal conductivities of the materials were considered, the loss by radiation being negligible. He showed that the useful work done externally attains a maximum when the external resistance equals the inter-

²This Bulletin, 9, p. 77; 1912.

³Rayleigh: Phil. Mag. (5), 20, p. 361; 1885.

nal resistance. He compared the mathematical expression for the external work with the energy dissipated by heat conduction in the elements. The ratio of these two quantities is the efficiency. He found that the efficiency of the thermopile does not depend upon the absolute dimensions (cross sections) of the elements, or of their thermal and electrical resistances, but only upon the ratios of these quantities. The efficiency of the thermopile is independent of the number and lengths of the elements, and of the temperature difference of the junctions; it is dependent only upon the thermoelectric power of the single elements. The conclusion arrived at was that a thermopile would be far less efficient than a dynamo and steam engine. Kollert⁴ also found that the efficiency of the thermoelectric generator does not depend upon the number or dimensions of the elements. In the generators tested by him the source of heat was a series of bunsen burners. He found the efficiency of the various types of thermoelectric generators to be from 5 to 12 per cent.

Hoffmann⁵ investigated experimentally the effect of the loss of heat by radiation and by conduction upon the efficiency of the thermopile. He arrived at practically the same conclusions as did his predecessors.

An important contribution to the discussion of the efficiency of thermopiles is by Altenkirch.⁶ He neglects the Thomson effect for small temperature differences and sets the thermal emf proportional to the temperature difference. He found that (1) the efficiency is independent of the number of junctions, (2) the most favorable conditions are obtained when the ratio of the electrical resistance to the heat conductivity is the same in both wires, (3) for small emfs the electrical energy developed increases as the square of the emf, but for large⁷ emfs the Peltier effect must be considered. (4) The external resistance may be two or three times the internal resistance without seriously affecting the maximum efficiency of the thermopile. The last deduction is of interest in view of the generally accepted notion that it is very essen-

⁴ Kollert: *Elektro-Tech. Zs.*, 11, p. 333; 1890.

⁵ Hoffmann: *Inaug. Diss.* Rostock; 1898.

⁶ Altenkirch: *Phys. Zs.*, 10, p. 560; 1909.

⁷ It will be shown on a subsequent page that the increase in radiation sensitivity is far from being proportional to the increase in emf, when a comparison is made of a bismuth-silver and a bismuth-iron thermopile.

tial to have an exact equality of internal and external resistance. He gives a series of curves showing the efficiency of the thermopile for different values of thermoelectric power, and for different values of external resistance. These efficiency curves are very flat at the maximum and they are far less symmetrical than the herein-described observations, which show that the radiation sensitivity of the thermopile is the same when the (external) galvanometer resistance is one-half, or twice the resistance of the thermopile.

The aforementioned discussions relate to thermopiles which are to be used as thermoelectric generators to replace the dynamo. The most recent theoretical contribution on the construction of thermopiles for measuring radiant energy, and relating especially to vacuum thermopiles, is by Johansen.⁸ His assumptions and conclusions do not differ radically from those of his predecessors. His deductions are that (1) the galvanometer resistance should be equal to the resistance of the thermoelements; (2) the radii of the two wires of the thermoelement should be so chosen that the ratio between the heat conductivity and the electrical resistance is the same in both; (3) the heat loss by conduction through the wires must equal the heat loss by radiation from the junctions (a question that can be answered only by direct experiment with the material to be used); and (4) the radiation sensitivity is proportional to the square root of the exposed surface. In his experimental instrument, the "cold" (unexposed) junctions are joined directly to the binding posts. This is likely to cause a "drift" of the zero reading owing to the fact that the air is warmed by the incident radiation and the "cold" junction can not quickly assume the temperature of the surrounding air. In a subsequent paper⁹ he recognizes this defect, and gives a symmetrical design with circular receivers as obtained in the Rubens thermopile.

He makes further computations showing that in the unsymmetrical type of thermopile the radiation sensitivity is $\sqrt{2}$ times that of the symmetrical design. In other words, his unsymmetrical design should be about 40 per cent more sensitive than the Rubens thermopile and the herein-described thermopiles.

⁸ Johansen: *Ann. der Phys.* (4), **33**, p. 517; 1910.

⁹ Johansen: *Phys. Zs.*, **14**, p. 998; 1913.

Johansen states that using an iron-constantan element the Peltier effect decreases the deflections by $\frac{1}{4}$ per cent and is of no consequence so long as the same resistance is in the circuit. In an iron-bismuth element the Peltier effect is four times as large, i. e., one can observe with an accuracy of 1 per cent when the external resistance is varied. This estimate is in agreement with previous computations¹⁰ which indicated a correction of about 1 part in 300 for iron-constantan. On the same basis of computation an error of about 1 part in 150 would result in the galvanometer deflections when using bismuth and silver for the thermal element. However, the amount of current flowing may be controlled by placing sufficient resistance in series to reduce all the galvanometer deflections to the same value. In this manner the Peltier effect will be the same for all intensities of the incoming radiation. By using a rotating sector to reduce the intensities of the radiations so as to produce approximately the same deflections, the relative values of the radiations will not be in error.

III. METHOD OF CONSTRUCTION

The method of construction of the thermoelements remain practically the same as previously described.¹¹ Silver wire is used with the bismuth because of its low resistance and because it is easily cleaned and annealed by heating it on a thin metal plate in a bunsen flame. Its weak point (which seems to be a common property of fine wires, e. g., Cu, Cd, etc.) is deterioration by the action of sulphides in the air. It is therefore given a thin coat of shellac, after mounting the elements and determining their resistance. The shellac becomes thoroughly baked upon the silver wires during the process of smoking the receivers over a sperm candle. This shellac does not affect, by a measurable amount, the sensitivity or heat capacity (hence quickness of action) of the thermopile. This was amply demonstrated by testing the sensitivity of a thermopile before and after shellacking the wires. Several thermopiles were constructed of bismuth and copper wires. The main obstacle experienced in construction was the difficulty in soldering the copper wires in case they became tar-

¹⁰ This Bulletin, 4, p. 402; 1907. ¹¹ This Bulletin, 9, p. 7, 1912; J. Franklin Inst., 172, p. 559, 1911.

nished. The sensitivity was as high as that of the bismuth-silver thermopile.

The method of joining the bismuth and the silver wires by means of the V-shaped, electrically heated, nichrome wire is continued as described in the previous paper. No difficulty is experienced in handling silver or copper after annealing. The best results are obtained by attaching a bead of tin about 0.05 mm diameter on the end of the silver (or copper) wire. The simplest procedure is to cut the wires the proper length (Bi, 3.5 mm; Ag, 10 to 12 mm). All the subsequent operations are performed upon a pad of clean white paper. A reading glass is used to magnify the objects. First the beads of tin are attached to the silver wires and trimmed to the proper size. The silver wire is then held secure by covering nearly the whole length of it with a small metal weight (say, a block of brass 4 by 5 by 15 mm), the bead of tin protruding. By means of a light, flexible, fine-pointed tweezers one end of the short bismuth wire is held in contact with the bead of tin and the two are melted together by touching the silver wire, close to the bead, with the nichrome heater. This silver wire, with the bismuth wire attached thereto, is then seized with the tweezers and the free end of the bismuth wire is melted to another silver wire. An appreciable tensile stress is then applied to determine whether the juncture is strong. The actual amount of tension is learned by experience; usually the juncture, which is an alloy of bismuth and tin, is stronger than the bismuth wire. These elements are then held secure by means of the brass weight already mentioned. The rectangular receiver is pushed under the juncture and is melted thereto by touching it lightly with the nichrome heater. These tin receivers are best handled by means of wooden toothpicks which are cut flat and pliable at one end, and moistened to hold the metal plate in transferring it. A speck of rosin placed on the receiver causes the bismuth to fuse to the tin over the greater part of its length. This warms the wire near the juncture thus compensating somewhat for the heat lost by conduction along the wire, and it seems to increase the radiation sensitivity. That the heat loss by conduction along the wire is appreciable is shown by exposing 0.5 to 1 mm length of the bismuth wire which extends beyond the edge of the receiver. Using a

black background to prevent reflection of radiation from the rear, upon the thermopile, the sensitivity is higher than when only the receiver is exposed. This demonstrates also that the bismuth wires are sufficiently long so that the cold junctions are not appreciably heated by conduction from the exposed junctions. When the slit is considerably narrower than the receiver the sensitivity is somewhat reduced, owing to the fact that the whole receiver is losing heat by convection and by radiation, while only part of the receiver is receiving heat. Hence it is desirable to design the width of the receiver for the problem under investigation.

In the first thermopiles constructed the entire rear surface of the receivers was given a thin coating of shellac. As experience was gained it was found that putting shellac on the overlapping edge of the receiver was sufficient for insulation. After mounting them, the central line of receivers was caused to adhere by moistening the shellac with alcohol. The insulation tests were made before and after a series of receivers were in contact. In this form of linear thermopile, having bismuth wire 0.1 mm diameter, silver wire 0.036 mm diameter, and receivers of tin 0.02 mm in thickness (this sheet tin is obtained from the ordinary "paper" condensers used in telephone service), the time required for the galvanometer to register a maximum deflection was about twice the time of single swing of the galvanometer, i. e., using a 3-second single swing on open circuit, the maximum galvanometer deflection was attained in 5.5 to 6 seconds after exposing the thermopile to radiation.

As shown in Figs. 1 and 3 the ends of each thermoelement are soldered to small (0.5 mm) copper binding posts. This enables one to test the resistance (0.41 to 0.45 ohms for bismuth 0.1 mm in diameter) of each thermoelement, and renders it convenient to replace defective or broken elements.

Receivers with thermal elements in series-parallel.—As the construction of thermopiles progressed it was found that, provided there were sufficient thermoelements per unit area of receiver so that there was no lag in equalizing the temperature over the whole absorbing surface, there was no appreciable gain in sensitivity by increasing the number of thermoelements within a given area of receiver. This is owing to the fact that there is an optimum size

of receiver which absorbs at a sufficient rate to compensate for the losses by radiation from the surface and by conduction along the wires. Using bismuth wire 0.06 mm diameter there is but little gain in placing more than 2 junctures per 1 mm length of receiver;

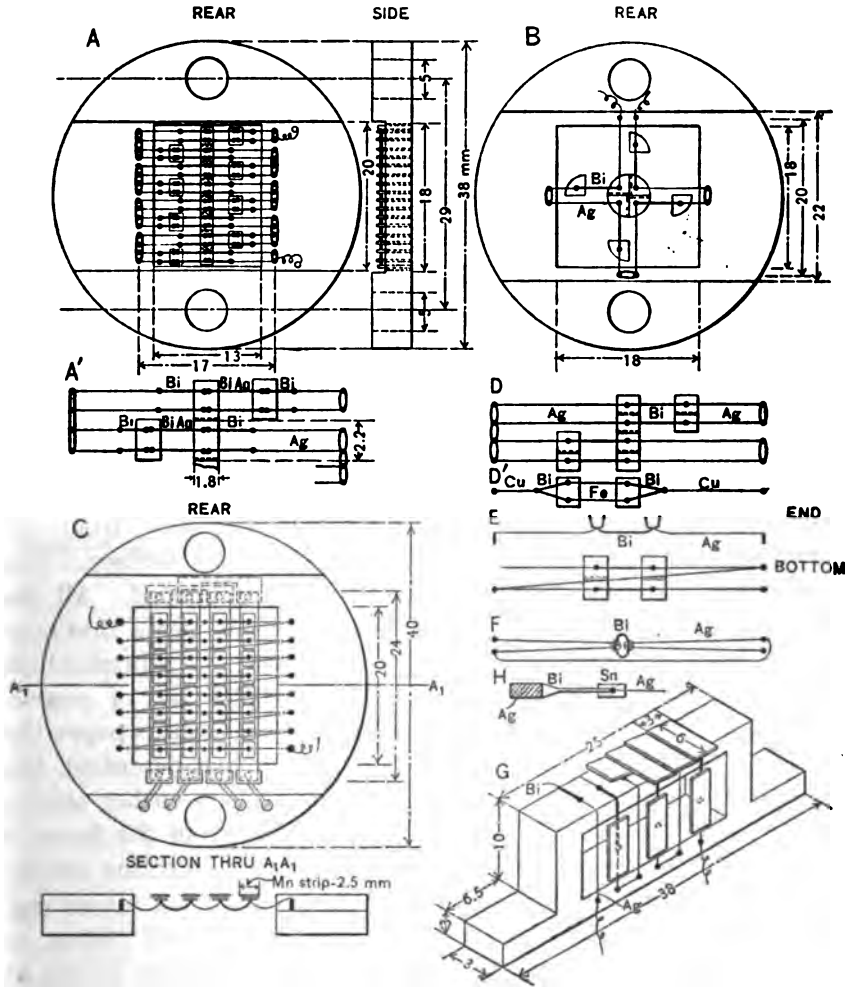


FIG. 1.—Various designs of thermopiles

and there is a decided loss in sensitivity by using only 1 juncture per 1.2 mm length. On the other hand, using bismuth wire 0.1 mm in diameter there was no gain in placing more than 2 junctures per 1 mm length of receiver; and there was no appreciable loss in

sensitivity by having as few as 1 juncture per 1.5 mm length of receiver. The next step was to further shorten the time to attain a maximum deflection and to reduce the internal resistance. By attaching two thermoelements to one receiver as shown in Fig. 1A, and in illustration No. 1 of Fig. 3, the number of overlapping receivers is reduced by one-half. This reduces the superfluous metal at the lap, and also the amount of insulation. The time required to attain a maximum deflection was reduced from 2 to 1.3 times that of the single swing of the galvanometer.

The dilute alcoholic solution of shellac used for insulation is applied to the overlapping edge with a fine-pointed toothpick. It is also applied to the silver wire on the receiver, and after mounting, the whole silver wire is covered with shellac. The front side is given a thin coat of a mixture of lampblack and platinum black in alcohol, with sufficient turpentine to make it adhesive. The finest grained material is applied, the coarsest material having settled to the bottom of the container. The thickness of the layer is just sufficient to cover the bright metal as viewed in the sunlight. This blackened surface is then smoked over a sperm candle as previously described. Usually the shellac, from the insulating joints, melts and makes a smooth black surface. The smoking is therefore continued until this is obliterated. All the soot is then brushed off with a fine-haired brush, and a thin coat of soot is again applied. If this becomes dusty, it is brushed off and the surface is resmoked. The paint below it, of course, remains intact. In all the thermopiles discussed in this paper the receiving surfaces were smoked in the manner just described, the final thin coating of soot being deposited from a rather smoky flame. The fine-grained "hard" bluish smoke from the flame is not used because it is grayish and has a higher reflecting power. The radiation sensitivity is surprisingly constant on resmoking. The smoke is produced by holding a sheet-iron funnel (about 10 cm long and 5 cm in diameter at the base with a slit 2 by 10 mm at the top) over a sperm candle.

By joining two elements in series-parallel the internal resistance is reduced to one-fourth that which would obtain in thermopile having all the elements in series. The emf is reduced by one-half, but, as will be shown presently, the radiation sensitivity is unaffected. In case one uses a potentiometer or a moving coil gal-

vanometer, it is of course desirable to use a great many elements in series in order to attain a high emf.

In the series-parallel form of thermopile the radiation sensitivity was increased 10 to 12 per cent over the average sensitivity of the previous design. Using a galvanometer single swing of 3 seconds the maximum deflection is attained in 3.8 to 4 seconds and 92 to 95 per cent of the maximum deflection is attained in 2 seconds. The zero reading is very constant in both forms of thermopiles. Frequently the cause of zero shift is to be located in the warming of the jaws of the slit (or of the window, if any be used) by the incident radiation. The jaws of the slit should therefore be of metal and they should be sufficiently massive to prevent an appreciable rise in temperature. In some of his most sensitive spectral thermopiles the writer uses a double-walled slit. The outer one is made of thin sheet copper which is cut to fit the curvature of the spectral lines.

In the series-parallel arrangement the two elements are fused to the receiver in the same manner as was described for attaching the single elements. The silver wires are attached to the copper posts (previously covered with solder) by means of Wood's alloy, which is used freely to connect the four posts as shown in Fig. 1A. The silver wires are sufficiently long to cross the four posts. They must be untarnished, otherwise the Wood's alloy does not make good contact and an extra resistance, of 0.1 ohm or greater, is introduced.

With reference to the reflecting power of the lampblack paint and the superficial layer of soot it may be added that such a surface is nonselective (i. e., it has no narrow absorption bands) and practically uniformly absorbing throughout the spectrum.¹² In the surface thermopiles previously described¹³ no receivers were attached to the unexposed junctions, and no provision was made for air circulation near them. In Fig. 1G is shown a design which embodies these improvements. It is important to have the exposed and the unexposed junctions symmetrical in size and in emissivity so that they will come to the temperature of the surrounding air (which is warmed by the incident radiation) at a uniform rate and thus avoid drifting of the zero reading of the galvanometer.

¹² This Bulletin, 9, p. 283; 1913.

¹³ This Bulletin, 9, p. 7; 1912.

IV. EXPERIMENTAL TESTS OF RADIATION SENSITIVITY OF THERMOPILES

Under this heading are collected the most important and the most crucial experimental tests relating to the various factors which affect the sensitivity of thermopiles which were fully completed, mounted, and ready for use. In the preceding paper¹⁴ some of the tests were made on single thermocouples and the results attained were not always consistent with those observed on completed instruments. This was to be expected, for in assembling the single thermocouples into a complete instrument, the emissivity was changed.

The radiation sensitivity as a function of the area exposed.—In the single thermocouples the tests showed that the sensitivity was not proportional to the square root of the area exposed to radiation, but that the area had an optimum value which gave a considerably higher sensitivity than required by the square-root law. From this it appears that the highest sensitivity is attained by building up a composite receiver of elements having individual receivers of a size giving the optimum sensitivity. Just how much greater this sensitivity will be than that attainable by using a less favorable size of receiver is undetermined. From the data previously published the expected gain may amount to 50 per cent. The estimates of increased sensitivity given in the preliminary publications¹⁵ are evidently too high. It was there stated that a receiver 4 mm in length built up of 4 individual receivers, 1 by 1 mm in area, would be twice as sensitive as a single receiver 4 by 1 mm in area. The sensitivity of a receiver composed of 4 parts, 1 by 1 mm in area, is not four times that of one of its components, 1 by 1 mm in area. It is only twice (square root of the total area exposed) that of the unit area, as is well illustrated on a subsequent page (see Fig. 6). In the case of the single receiver 4 mm in length, as compared with the composite receiver of 4 elements 1 mm in length, the gain in sensitivity in the latter is the part contributed by the small receivers being of a size which gives an optimum sensitivity as compared with the 4 mm length which falls below the square-root law in sensitivity. This optimum size

¹⁴ This Bulletin, 9, p. 7, 1912; Phys. Zs. Zeit., 14, p. 683, 1913.

¹⁵ J. Franklin Inst., 175, p. 497, 1913; Zs. Instrumentenkunde, 34, p. 14, 1914.

of receiver arises from the fact that a minimum area of receiver is required which absorbs radiant energy at a sufficiently rapid rate to compensate for the loss of heat by conduction along the wires. On the other hand if the receiver is large the loss by radiation from the receiver is more important than that of conduction along the wire (and there is also a lag in attaining thermal equilibrium in the receiver) owing to the lag in heat conduction from the remote edges which are at the highest temperature. Using bismuth wire 0.1 mm in diameter the minimum area of the receiver giving the highest sensitivity is of the order of 1 mm².

In the thermopiles first constructed 1 thermoelement was placed per 1 mm length of the completed receiver. This number was increased to 2 elements (several thermopiles¹⁶ had 22 elements in 10 mm length of completed receiver), and while fortunately the sensitivity was not decreased, it was usually not very markedly increased (owing to the extra insulation and heat capacity) as compared with the thermopile having a smaller number of elements. On the other hand it was found that when there was but one element per 1.5 mm length of the finished receiver, the time for attaining a maximum deflection was increased owing to the slowness of heat conduction from the extreme edge and the consequent delay in attaining temperature equilibrium in the receiver. In the thermopiles constructed of bismuth wire 0.1 mm in diameter and silver wire 0.036 mm in diameter it was found that the radiation sensitivity was practically the same for one thermoelement per 0.8 to 1.2 mm length of the completed receiver. The usual width of the individual receivers was 1.5 to 1.8 mm and the length was 1.0 to 1.1 mm. In thermopiles constructed of bismuth wire 0.06 mm and silver wire 0.03 mm in diameter, this tolerance was not so large, the best length of the individual receiver being of the order of 0.5 mm to 0.8 mm. In the thermopiles having all the elements in series the time required for attaining a maximum deflection was about twice the time of single swing of the galvanometer. This was found true for a galvanometer swing of 2.5 to 5 seconds. In the new design Fig. 1A, in which two elements are joined in series-parallel, less shellac is required

¹⁶ This Bulletin, 9, p. 283, 1913. This thermopile No. 6, having a resistance of 10.8 ohms, had a receiving surface 5 mm wide, no receivers were used on the unexposed junctions.

for insulation, there is less inactive metal in the lapping of the adjacent receivers, and the time required to attain a maximum deflection is reduced to less than four-thirds the time of single swing of the galvanometer. The receivers are 1.5 to 1.8 mm wide and 2.2 mm long; and the radiation sensitivity is the highest yet attained.

The radiation sensitivity as a function of thermal conductivity and of emissivity.—It is of interest to cite the behavior of several thermopiles to illustrate the marked effect in sensitivity that may be experienced by deviating from the general method of construction. For example, the central line of receivers of one thermopile (No. 10; 22 junctions of bismuth wire 0.06 mm and silver wire 0.03 mm; resistance 22 ohms; receivers 0.9 by 1.5; area exposed 1.5 by 10 mm) was given an additional coating of shellac to cause the individual receivers to adhere, instead of resorting to the usual method of moistening the insulating layer of shellac with alcohol. The instrument was slow in response to a radiation stimulus, and it was insensitive. This extra shellac was then removed (by means of blotting paper wet with alcohol) and on resmoking it the radiation sensitivity was increased by 48 to 50 per cent. It was then as quick acting as the best series-parallel thermopiles of later construction, and it is the most sensitive of all the thermopiles constructed of bismuth and silver.

Another example, which best illustrates the effect of emissivity upon sensitivity, is a thermopile (No. 21), constructed of 0.1 mm wire pressed flat to reduce thermal conductivity to the cold junction. It consisted of 28 junctions in a receiver having a length of 14.5 mm (width of receiver 2 mm; resistance 13.5 ohms). A test on a single junction of flat bismuth wire against a junction of the round wire (to which was attached a tin receiver) indicated a higher sensitivity for the flat wire. In the completed thermopile, however, the radiation sensitivity was 25 to 30 per cent less than the average sensitivity of a number of thermopiles constructed of the round wire, all of which thermopiles had closely (2 to 3 per cent) the same sensitivity. A test of the insulation showed that the individual receivers were in normal condition. Resmoking the surface did not change the sensitivity in a marked degree, and it was concluded that this lowering of the sensitivity was

owing to the increased emissivity of the flat wires which presented an additional surface for radiation. This could be avoided to some extent by using fewer elements. This thermopile was unusually quick in its action, owing no doubt to reduction of thermal conduction along the wires. Thermopiles constructed of bismuth wires 0.15 mm in diameter, which were pressed flat, were found to be very fragile, and hence this mode of construction is not to be recommended.

A test was made of the radiation sensitivity of an element in which the receiver was a flat piece of bismuth. For this purpose one end of a bismuth wire 0.15 mm in diameter was pressed flat, as shown in Fig. 1H, and the silver wire was attached to it with Wood's alloy. To the other end of the wire (which was round) the silver wire and the tin receiver were attached in the usual manner. An area of the flattened bismuth, the size of the tin receiver was painted black. Assuming equality of the exposed areas, the receiver of flattened bismuth wire was 15 per cent more sensitive than the junction of round wire having the tin receiver; but it was defective in that it lagged in attaining temperature equilibrium when exposed to radiation.

Relation between external and internal resistance of a thermopile.—

In a previous paper¹⁷ it was found when the three units of a large surface thermopile were connected in series, thus producing an internal resistance which was about 6.4 times the external (galvanometer) resistance, that the radiation sensitivity was only about two-thirds (value plotted as a triangle, Δ , in Fig. 2) that of the thermopile having the units joined in parallel, when the resistance was practically the same as that of the galvanometer.

In the recent experiments the external resistance was greater than the internal (thermopile) resistance. The data obtained in these experiments relate to 3 thermopiles and 2 galvanometers. Their importance will be evident from the fact that one of the first specifications of intending purchasers is that the resistances of the thermopile and the galvanometer must be equal. The most important tests of the sensitivity of a thermopile as a function of the external (galvanometer) resistance was made on the large thermopile shown in illustration No. 2 of Fig. 3. Its battered

¹⁷ This Bulletin, 9, p. 7; 1912.

condition is owing to the hard usage given it as described below. This thermopile, No. 26, was constructed of bismuth wire 0.1 mm in diameter (length 5 mm) and silver wire 0.038 mm in diameter. The individual receivers of pure tin were 3 by 1.5 by 0.02 mm, the central receiver being 3 by 23.6 mm. There were 18 junctions, the total resistance being 13.95 ohms. Two additional lead-wires were soldered to the thermopile; at the fourth and tenth junction. In this manner it was possible to study the behavior of 4, 6, 8, 10, or 18 elements; having resistances (approximate) of 3.1, 4.85, 6.15, 7.85, and 13.95 ohms respectively. This thermopile was constructed for the "absolute radiometer" (see VIII) described on a subsequent page. It was discarded for that particular work because it had a slight shift of the zero reading ("creeping") after exposing it to radiation and because it was not as quick acting as was desired for absolute measurements. The slowness of response seemed to be due to the large receivers which, owing to the slowness of heat conduction from their extreme edges, lagged in attaining thermal equilibrium. This, however, did not interfere in making the following tests.

The galvanometer which was used in these tests consisted of four 26-ohm coils mounted in Swedish iron shields¹⁸ as described in Note II. When the four coils were joined in series-parallel (26 ohms) the current sensitivity was twice that of the four coils in parallel (6.5 ohms). When all four coils were joined in series (104 ohms) the current sensitivity was not quite (about 1 per cent less than) four times that of the four coils in parallel (6.5 ohms); the complete period in all cases being the same, viz, four seconds.

Since the efficiency of the galvanometer is not under consideration we need not give it further discussion. The test is for conditions such as would be experienced in the average laboratory. It is assumed tentatively that the best conditions obtain when the external and the internal (thermopile) resistances are equal. The galvanometer period was kept constant, and the thermopile was exposed to a standard of radiation,¹⁹ consisting of a seasoned incandescent lamp operated at a constant temperature. In establishing this radiation standard it was found that the sensitivity of

¹⁸ This Bulletin, 9, p. 7; 1912.

¹⁹ This Bulletin, 11, 1914; J. Franklin Inst., 176, p. 219, 1913.

the thermopile was independent of the energy absorbed by the receiver. This test was applied by exposing the thermopile to a black body heated from 600 to 1100° C., and the galvanometer deflections were found to be proportional to the energy falling upon the receiver.

Using a thermopile (No. 25) having a resistance of 11.3 ohms, the same galvanometer deflection was observed when the galvanometer resistance was 26 ohms as when it was 6.5 ohms. In other words, the radiation sensitivity was the same when the external resistance was one-half and when it was twice the resistance of the thermopile. Exactly similar results were obtained with a thermopile (No. 23) having a resistance of 9.4 ohms when used with a

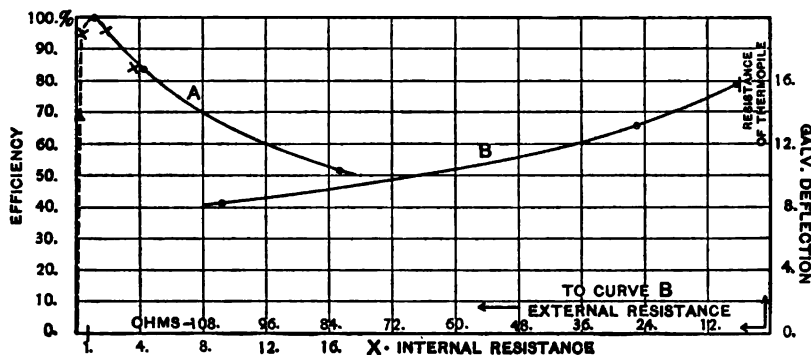


FIG. 2

four-coil galvanometer having a resistance of 5.3 ohms (coils all in parallel) and 21 ohms (coils in series-parallel).

Using 9 junctions of the thermopile (No. 26) just described having 6.9 ohms (and a galvanometer resistance of 26 ohms), the radiation sensitivity (galvanometer deflection) was about 17 per cent less than that observed with a galvanometer resistance of 6.5 ohms. This test was repeated using 8 junctions of this thermopile giving a resistance of 6.2 ohms. The results are given in Fig. 2. Curve B gives the galvanometer deflections (ordinates) and the external resistance. Curve A gives the loss in sensitivity ("the efficiency") in per cent when the external resistance (the abscissæ) is x -times the internal resistance, the efficiency being taken a maximum (100 per cent) when $x = 1$. The crosses (x. x) are

for the subsidiary tests mentioned in the text. The results show that the galvanometer resistance may be twice the resistance of the thermopile (a condition one would not meet frequently in practice) without seriously affecting (decreasing by 5 per cent) the efficiency of the instrument. These results are in fair agreement with the theoretical deductions of Altenkirch,²⁰ summarized on a preceding page.

During the past few years more than two score thermopiles and half a score of galvanometers have been constructed. The experience gained shows that the radiation sensitivity of the thermopile is dependent primarily upon the nicety of construction of the receivers and of the thermojunctions; and the galvanometer sensitivity is mainly a question of nicety of construction of the suspended system. If the voltage is to be measured with a potentiometer, then it is, of course, desirable to have a large number of elements joined in series. If the thermopile is to be used with a d'Arsonval galvanometer, it will be advantageous to have all the elements in series. In this manner there will be a gain in voltage and the increase in resistance of the thermopile may be utilized as part of the external, critical damping-resistance of the galvanometer. If the galvanometer is used as an ammeter, as is the usual custom, then the thermoelements are to be joined in series-parallel to produce a resistance of the same magnitude as that of the galvanometer. In this connection a single receiver, with several junctions of bismuth attached to it (to eliminate the lag of thermal conduction along the receiver), would no doubt be just as efficient when connected with a galvanometer of very low resistance.

Thermoelectric power of bismuth-silver.—The thermoelectric power of silver is low, and different samples were found to have the same value.

The thermoelectric power of various samples of bismuth wire was found to differ considerably. Of the eight samples tested (having diameters 0.06, 0.08, 0.1, and 0.15 mm) the thermoelectric power, against silver, varied from 75 to 82 microvolts. This seemed to depend upon the purity of the material, as indicated by the purchases at different times. The bismuth wire received in

²⁰ Altenkirch: *Phys. Zs.*, 10, p. 560; 1909.

one order of 0.08 and 0.1 mm had a thermoelectric power of 76 microvolts, while another order consisted of material giving, respectively, 75 and 82 microvolts. The resistance of the different samples of material was found quite constant, being of the order of 0.11 ohms per millimeter length of wire 0.1 mm diameter.

V. A THERMOPILE OF BISMUTH ALLOY

The most recent investigations of Haken,²¹ and of Gelhoff and Neumeier,²² show that an alloy of Bi + 9 to 10 per cent antimony has a thermoelectric power which varied from 77 to 87 microvolts. The writer has found, however, that alloys containing more than 5 per cent of antimony are too brittle for thermopiles. Moreover, different samples and different melts of the same sample of this alloy (supposed to contain the same amount of antimony) did not give the same thermoelectric power which varied from 61 to 85 microvolts. Apparently the physical structure has an influence upon the thermal emf. In cooling after casting the molten material upon a glass plate (as will be described presently) the antimony separates very easily from the bismuth and the alloy must be heated considerably above its melting point in order to form an intimate mixture, which is shown by the production of a smooth bright surface on the molten material. There is no special reason for using an alloy of bismuth instead of the pure bismuth, other than that it can be more easily soldered with Wood's alloy, which if too warm alloys with and renders pure bismuth too brittle for thermopiles. This alloy was therefore discarded and pure bismuth wire was employed as in previous thermopiles, because the best bismuth wire against silver has a thermal emf of +81 microvolts per degree.

Tests showed that an alloy of bismuth containing 5 to 6 per cent of tin had a uniform (for different melts) thermal emf of -44 to -45 microvolts per degree. A thermoelement consisting of the best bismuth, and an alloy of Bi + 5 to 6 per cent tin gives a thermal emf of 125 to 127 microvolts per degree.

The bismuth and bismuth-tin alloy may be obtained from Hartmann and Braun in fine pliable wire from 0.06 to 0.15 mm diame-

²¹ Haken, *Verh. Phys. Gesell.*, 12, p. 229; 1910.

²² Gelhoff and Neumeier, *Phys. Gesell.*, 15, p. 876; 1913.

ter. This may be further reduced in size by cutting the wire in short lengths and pressing it flat between plates of glass. These flat pieces are then cut into narrow strips of the desired width.

The wire of bismuth-tin alloy may be made by allowing the molten metal to drop from a height upon a smooth perfectly clean glass plate²³ which causes it to spatter into thin flat threads.

Pfund²⁴ goes a step further, producing much longer filaments by hurling the molten metal over a glass plate. The spattering material is quite pliable. The wide strips increase the emissivity, so that for the same resistance of the round as compared with the flat material, the best width to balance emissivity and conductivity must be found by experiment.

A thermopile was constructed as shown in Fig. 1A. The receivers were of platinum 0.005 mm in thickness and 1.8 by 2.5 mm in area. The heat capacity of this receiver, exclusive of the alloy wires, was a trifle less than that of the tin receivers. Hence its slow action to be mentioned presently must be attributed to the great heat capacity of the alloy wires. The bismuth wire was 0.1 mm diameter; the alloy was selected and estimated of a slightly greater area of cross section. The thermopile was constructed by melting a globule of pure tin (0.05 mm in diameter) to the receiver, using soldering solution to cause the tin to adhere to the platinum. The free end of the bismuth wire (joined to the silver wire by means of a tin bead as described in previous publications) was joined to the tin on the receivers. The wires of bismuth-tin alloy were then placed on the receivers (see Fig. 1A) and secured with Wood's alloy, care being taken that the fusible alloy did not affect the bismuth wire, thus producing a brittle juncture. The end wires were attached to the binding posts by means of Wood's alloy. The front side of the receivers was painted with a mixture of lamp black and chemically precipitated platinum black, as previously described,²⁵ and smoked with soot from a sperm candle.

Two elements were joined in series-parallel, thus reducing the resistance by one-fourth from what would be obtained by joining all the elements in series. The silver or copper end wire is used for three purposes: (1) to maintain a low resistance, (2) to maintain symmetry by having all the high emf junctions close together,

²³ This Bulletin, 7, p. 248; 1910. ²⁴ Pfund: *Phys. Rev.*, 34, p. 228; 1912. ²⁵ This Bulletin, 9, p. 7; 1918.

freely in contact with the air, (3) to secure greater strength. The bismuth wire can not be easily attached to binding posts, and although pliable it is not advisable to subject it to torsional strains. The additional length of wire (of negligible resistance) at the ends of the bismuth adds pliability, which is needed in a commercial instrument subjected to rough usage. No shellac was used except for covering the silver wire and for insulation at the overlapping edges of the central line of receivers.

The radiation sensitivity of this thermopile was not quite as high as it was hoped to attain; neither was it as quick acting as the thermopiles of pure bismuth containing less metal in the receiver. However, as a first attempt at this design, the knowledge gained indicates where improvements may be made by using finer wires of the alloy. The resistance of this thermopile was 3.8 ohms. The thermal sensitivity (thermoelectric power) was about 55 per cent greater than the bismuth silver thermopile. The radiation sensitivity was 20 to 21 per cent²⁶ greater than the average sensitivity of a number of bismuth-silver thermopiles of the type having all the elements in series, and only 4 to 5 per cent more sensitive than the best thermopiles of bismuth silver having two elements joined in series-parallel. For some researches it will be of advantage to construct a thermopile of bismuth-tin alloy. However, from the results obtained with this thermopile it is evident that the radiation sensitivity is more dependent upon fineness of material, smallness of heat capacity, and neatness of construction than upon the thermoelectric power of the material used.

VI. A THERMOPILE OF BISMUTH IRON

The first metal tried with bismuth was iron, but it proved a failure²⁷ owing to the use of Wood's alloy, which produced a brittle juncture with the bismuth. After gaining the experience in constructing more than two score linear thermopiles, including every design mentioned in this paper, it seemed but fair to make another test of the combination of bismuth and iron. The iron used had a thermoelectric power of +13.5 microvolts against silver as com-

²⁶ In the preliminary note (Amer. Phys. Soc., No. 28, 1913) the value of 30 to 31 per cent is given. This higher value is owing to the fact that no corrections were made for differences in external and internal resistance.

²⁷ This Bulletin, 9, p. 7; 1912.

pared with -80 microvolts for bismuth silver. The diameter of the bismuth wire was 0.1 mm, and that of the iron wire was 0.036 mm. The lengths of the wires were 3.5 mm for the iron and 3 mm for the bismuth. The latter wire was made somewhat shorter than usual, owing to the manner of construction, as shown in Fig. 1D'. For convenience in construction the two bismuth wires were joined in the form of a "Y" to a copper wire 0.08 mm in diameter. By introducing the copper wire all the high thermal emf junctures (bismuth iron and bismuth copper) are free in air and the resistance is kept low, as explained in Part V of this paper. The ratio of diameters of the wires is closely that required by theory. The receivers were of tin 2.0 by 1.8 by 0.02 mm as used in the bismuth-silver thermopiles. In fact everything was kept the same except the substitution of iron for silver, to determine the effect of the iron wire upon the sensitivity.

The thermopile was constructed in the same manner as described for the other thermopiles. The iron wires were cut to the proper lengths and pressed straight, but not annealed. A small globule of tin was then attached to the iron wire (as was done with the silver wire), the ends of the wire being first dipped in the zinc chloride solution. No difficulty was experienced in causing the tin globule to surround and adhere to the iron, as was experienced in the first work. This was owing to the fact that the wire was quite new and free from oxidation and tarnish. The bismuth wire was fused to the iron wire in the same manner as it was attached to the silver wire. In the completed instrument the iron wires were covered with shellac to prevent rusting. The completed thermopile consisted of 16 elements joined two in series parallel, forming a receiving surface 1.8 by 16.5 mm and having a resistance of 3.23 ohms. The resistance is therefore about 90 per cent higher than that of the bismuth-silver thermopile, constructed alongside with the one of bismuth-iron (bismuth wire 0.1 mm; silver wire 0.036 ; resistance of the 8 double junctions 1.84 ohms; area 1.8 by 16.7 mm).

The results of the sensitivity tests were rather disappointing, but they were not unexpected in view of the fact that the internal resistance was practically doubled while the thermal emf was increased only about 18 per cent. The sensitivity of the bismuth-

iron thermopile was 27 to 28 (arbitrary scale), which is 5 to 6 per cent below the average sensitivity of the bismuth-silver thermopile. The sensitivity of the bismuth-silver thermopile was 30 to 31, which was somewhat higher than the average sensitivity of the series-parallel design of bismuth-silver thermopiles.

The bismuth-iron thermopile was free from drift and appeared to have all the requirements of a good radiometer. From this it appears that but little gain was to be expected by bettering the workmanship, by constructing additional thermopiles of bismuth iron. The failure of the bismuth-iron thermopiles to show a higher sensitivity than the thermopile of bismuth silver appears to be due to the increased internal resistance of the former, which counteracts the sensitivity which is gained by increasing the thermoelectric power. From the experience gained with the thermopile of bismuth alloys no great gain in sensitivity was expected, but it seemed desirable to give the matter a fair trial. The only way to do so seemed to be to construct the complete instrument as used in practical work. In a preliminary test (using a juncture of iron and one of silver, with the bismuth wire between them; receivers of tin, 1 by 3 mm) the iron-bismuth junction was 28 per cent more sensitive than the one of silver bismuth. Here, of course, the internal resistance was the same for both junctions, and the sensitivity test applied to conditions which were different from those found in practice. In view of the general notion that a high thermoelectric power (without considering the specific resistance of the material) will produce a thermopile having a high radiation sensitivity, it is important to notice that this experiment is convincing proof to the contrary. As indicated by Haken ²⁸ the pure metals, not alloys, should be used; and from the herein-described experiments, bismuth (with its unusually high thermoelectric power as compared with its resistance) seems the most satisfactory of all.

Fine wires of copper, silver, iron, etc., seem unusually susceptible to corrosion, and the next step is to find a wire which is as easily handled as is silver, but which is free from corrosion. Gold and platinum are promising, but the latter has a high resistance and the

²⁸ Haken: *Verh. Phys. Gesell.*, 12, p. 229; 1910.

former becomes brittle when soldered with materials containing lead.

Probably the best combination producing a long-lived instrument is bismuth wire joined to the receivers as shown in Fig. 1D, with short wires of pure platinum (substituted for the bismuth in Fig. 1D') joined to a heavy (0.1 mm diameter) copper wire, as shown in the Y-form of Fig. 1D'. In this manner of construction it would be unnecessary to cover the wires with shellac to prevent corrosion. The coating of shellac, however, does not appreciably increase the heat capacity or emissivity of the wires. In fact, it seems to reduce somewhat the effect of convection currents, which, as is well known, are most effective upon very fine wires. According to the writer's experience, lacquers containing amyl acetate should not be applied to the bismuth juncture. The solvent of the lacquer seemed to attack the juncture, producing a high resistance.

VII. A RADIOMETER ATTACHMENT FOR MONOCHROMATIC ILLUMINATORS

At the present day visible and ultraviolet radiations are being extensively used as stimuli in biological, chemical, physical, and physiological investigations. As already stated, it is desirable in all cases to know the energy value (mechanical equivalent) comprised in the different wave lengths used as stimuli. For this purpose it is necessary to use a radiometer which functions independently of the frequency (wave length) of the stimulus. The most useful radiometer, which requires but little care, and which can be operated by experimenters having had but little experience in physical manipulations, is a thermopile. The bismuth-silver thermopile with its completely opaque (i. e., no openings in it) receiver is especially applicable to such radiometric measurements because of its high sensitivity and because it intercepts all the radiations falling within a given area. The latter is an important requirement²⁰ in radiometric measurements involving the relative amounts of energy in different parts of the spectrum, which energy distribution is affected by the change in focal length of the spec-

²⁰ See further J. Franklin Inst., 175, p. 497; 1913.

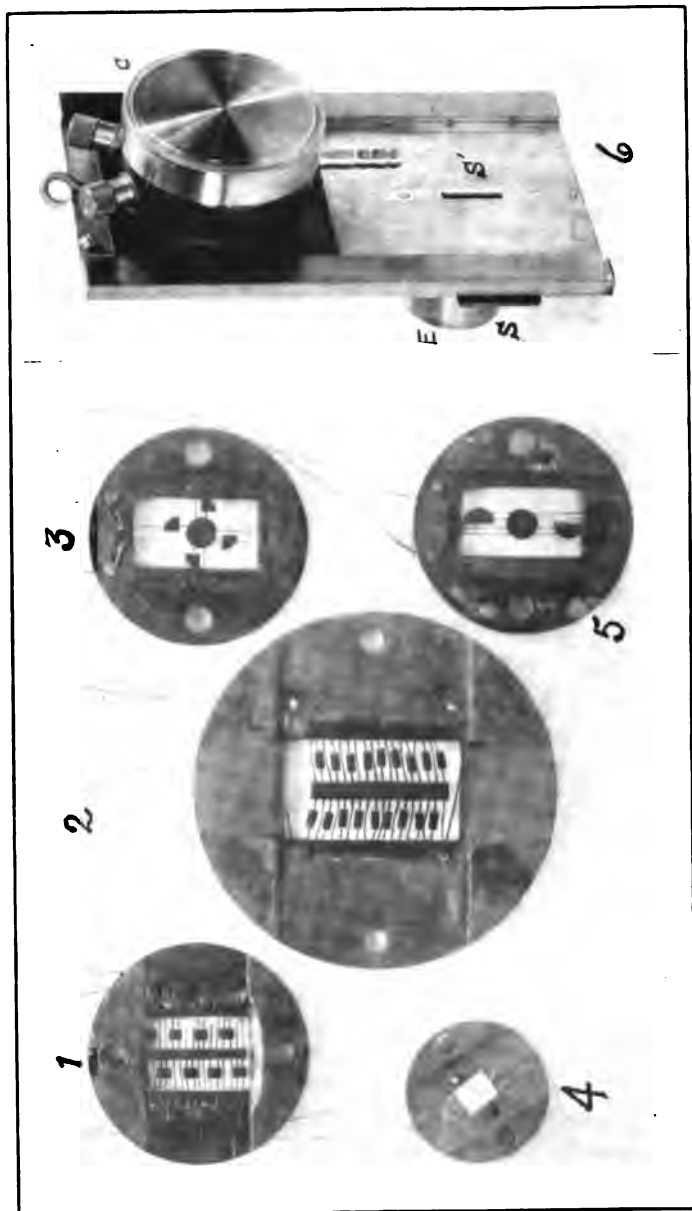


FIG. 3.—Various designs of thermopiles

trometer lenses. However, a knowledge of the distribution of energy in the spectrum of the source of radiation is generally not required in the measurement of light stimuli.

As an attachment to a monochromatic illuminator, the thermopile, Fig. 1A is mounted in a metal box B of Fig. 4 which can be closed air-tight by means of a cap, C, and evacuated through the outlet, D. A window, W, of quartz is placed over the slit. The metal box, containing the thermopile, moves in vertical ways, A, Fig. 4, which are attached to the adapter, E, thus displacing the eyepiece of the spectrometer. The slit, S, as constructed, is securely fastened to the telescope tube, thus preventing any accidental displacement of the thermopile in the spectrum. It was with the forethought of such a possible displacement, when the box is raised and lowered, that the slit was thus secured instead of attaching it to the box containing the thermopile. The jaws of the slit have their knife edges facing the incident radiations thus providing a sharp separation of the rays and thus eliminating a possible reflection of radiations from the slanting sides into the thermopile case. A somewhat better view of some parts of this attachment is shown in the photographic reproduction, No. 6, of Fig. 3, where the thermopile box is in the raised position, thus permitting the radiations coming through the exit slit, S, to pass out into space. In Fig. 3 the lettering corresponds with the lettering of similar parts in Fig. 4.

When it is desired to measure the intensity of the emergent radiations, the thermopile is lowered in front of the slit S, Fig. 3. When it is desired to have the light pass out into space, or when it is desired to make any adjustments or to test the calibration, the thermopile is raised above the slit as shown in Figs. 3 and 4. The "zero setting," say, upon the yellow helium line may be made as accurately within the slit, as it can be made upon a bolometer strip. For this purpose the small telescope or microscope used with the spectrobolometer, as previously described, is focused upon the slit (through S of Fig. 4). The slit jaws have, of course, been given the curvature of the spectral lines. The spectrometer circle is read, say, when the spectral line passes out of sight back of the right-hand jaw of the slit. The spectrometer circle is then read when the spectral line passes back of the left-hand jaw of the

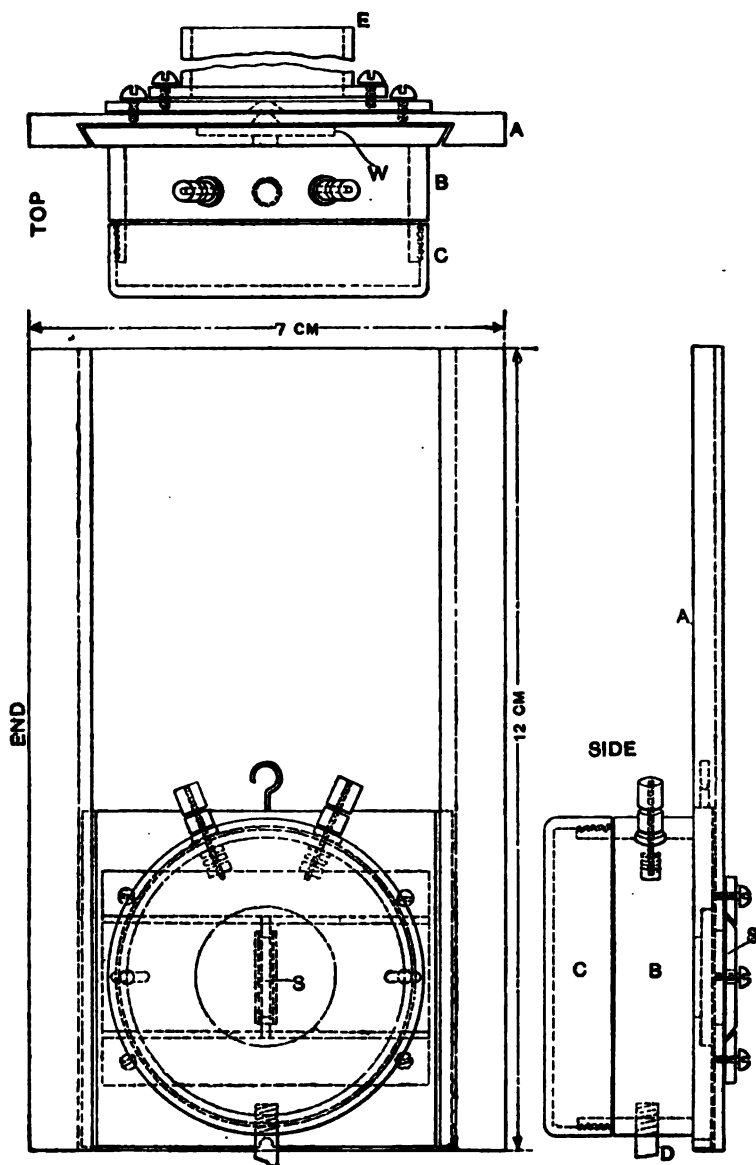


FIG. 4.—Radiometer attachment for monochromatic illuminators

slit. The spectrometer reading half way between these two points is the true setting to cause the spectral line to fall within the exit slit which is usually made the same opening as the collimator slit.

VIII. A THERMOPILE FOR ABSOLUTE MEASUREMENTS OF RADIATION

The pyrheliometer as designed by Ångström²⁰ consists of a thermoelement of iron and constantan attached to a thin strip of manganin (a thin layer of silk intervening for insulation) which acts as a receiver to intercept the radiant energy, and also as a heater through which an electric current may be passed to produce the same rise in temperature as that of the absorbed radiant energy. From the resistance of the strip, the electric current through it, and the area exposed to radiation, the absolute value of the radiant energy may be determined.

In this form of construction the manganin strip and the thermoelement may become separated, thus changing the sensitivity and the constants of the instrument. As mentioned in the preceding paper²¹ on radiation instruments, it was proposed to apply the bismuth-silver thermopile to this form of radiometer, which seems to have many commendable features. In the meantime Gerlach,²² at the suggestion of Paschen, has carried out a series of experiments and has obtained very satisfactory results with a modification of the Ångström radiometer. This modification consists in having the thermoelement (in reality a series of elements, a thermopile, of iron and constantan wires, with receivers rolled flat) detached from the heater-receiver of manganin, thus eliminating the possibility of variable contact. The thermopile is therefore heated primarily by radiation; but from the experience with the writer's design, this device is far more sensitive than ordinarily required and hence direct metallic contact is unnecessary. In fact for quickness of action and for electrical insulation it is desirable to have the manganin heater and the thermopile separated, to reduce the extra heat capacity of the insulating materials. Much of Gerlach's work having been published before great progress had been made on the most efficient form of the present

²⁰ Ångström: *Ann. der Phys.* (3), p. 294, 1890; (3), p. 663, 1899; *Phys. Rev.*, 1, p. 365, 1893.

²¹ This Bulletin, 9, p. 31, 1911.

²² Gerlach: *Ann. der Phys.* (4), 88, p. 1, 1912.

design, advantage was taken of his experience in making further improvements which consists principally in the construction of the heater-receiver. The thermopiles differ, of course, in that the one of bismuth silver has a continuous receiving surface, which increases the sensitivity. The sensitivity is also materially increased (doubled) by the use of bismuth silver instead of iron and constantan. In the Gerlach instrument the potential terminals are attached to the heavy copper electrodes supporting the thin manganin strip. About 1.5 mm of each end of this manganin strip is shielded from radiation. This amount of covering of the ends of the manganin strip was found experimentally to give uniform values to the constant of radiation. When the ends were not covered his values were smaller owing to heat conduction to the electrodes. As will be shown in a forthcoming paper dealing with radiation measurements, the measurement of the electrical energy expended in the whole strip and comparing it with the heat developed by radiation falling upon only part of the strip may give erroneous values.

In the present instrument the potential terminals are about 3 mm from the points where the ends of the thin metal strip are attached to the copper electrodes. The nichrome heater already described is used in soldering these wires. The potential wires are of fine platinum, 0.0055 mm in diameter. It is obtained from Wollaston wire having the silver removed from about 5 mm of the end which is attached to the receiver. There is practically no heat conduction along this fine platinum wire since the contact is a mere point on the longitudinal axis of the strip. The ends of the slit forming the opening in the receiver terminate directly over these potential terminals. Tests made with, and without, these coverings across the ends showed no observable difference in the radiation measurements. Provision has also been made to use the instrument without the slit jaws covering the strip. Using the receiver in this manner, the area of the strip exposed to radiation is defined by its full width, and by the distance between the potential terminals. A similar design of heater has been used by Bauer and Moulin²² as a source of radiation. By placing the potential terminals at a distance from the electrodes

²² Bauer and Moulin; *Compt. Rendus*, 149, p. 988; 1909.

the measurement of the electric energy put into the thin metal strip pertains only to that part which is exposed to radiation. The thermopile is somewhat shorter than this exposed strip and it is further protected by shields so that no radiation from that part of the strip, lying between the potential terminals and the electrodes, can fall upon the thermopile receiver. In fact the whole thermopile (excepting the central receiver) is covered with a thick screen of cardboard to provide electrical insulation and

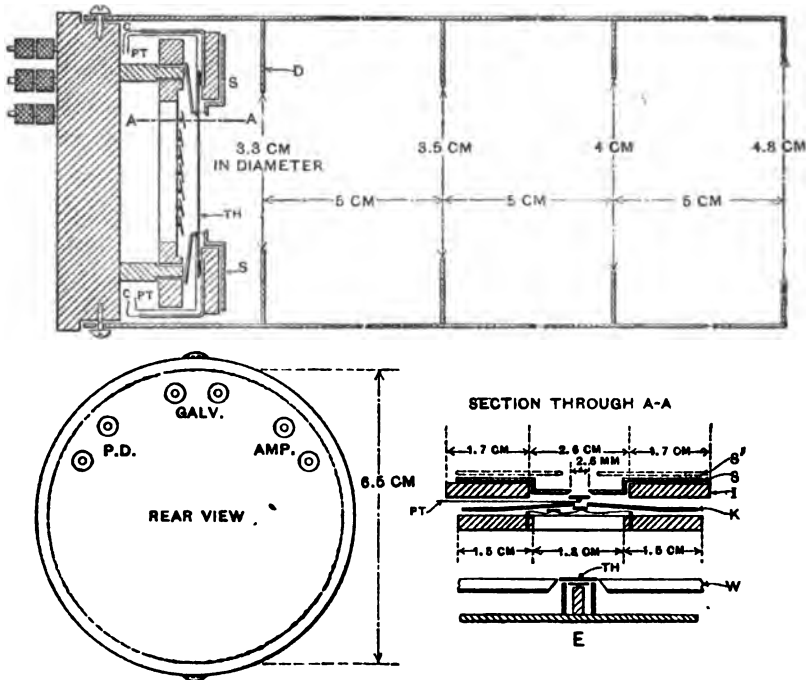


FIG. 5.—Thermopile for absolute measurements of radiation

to shield it from radiation. In front of the cardboard are two copper plates, K, 0.8 mm in thickness, which are painted black and smoked on the side facing the receiver-heater. In Fig. 5 are shown the essential parts of the thermopile as used in the absolute measurements. It consists of the slits, S, of brass or aluminum 1.2 to 1.8 mm in thickness. The insulating support, I, is of slate, upon which is mounted the "therlo," Th, manganin or platinum strip. The potential wires of platinum, Pt, are mounted on the

rear side of this receiver-heater. The electrodes, C, are of copper. One sample of "therlo," used was 5.5 mm wide, about 0.007 mm thick, 29.5 mm long between the electrodes, and 23.5 mm distance between the potential terminals. Using a receiver of bolometer platinum, which is much thinner than the "therlo" used, temperature equilibrium was attained in about 12 seconds. Some of the samples used were 4 to 5 mm in width. Receivers of bolometer platinum are much quicker than the thicker samples of "therlo" in attaining temperature equilibrium. However, the preliminary measurements of the Stefan constant of total radiation, as observed with these two kinds of receivers, are in excellent agreement.

In the lower right hand corner of Fig. 5 is given a section through A-A (viewed from above) which shows the arrangement of the slits, S, the receiver with its potential terminal, Pt, and the thermopile with the metal shields covering the cold junctions.

Four thermopiles were constructed before one was found as quick acting as desired. One of the thermopiles used in radiation measurements consisted of 10 double junctions joined in series-parallel as shown in Fig. 1D. In this instrument each receiver was 1 mm wide and two of these were joined in parallel instead of the design (Fig. 1A) in which two elements are joined to one receiver. This insures a stronger junction which is easily tested for tensile strength. The area of the central receiver was 1.8 by 18.6 mm. This receiver was raised about 1 mm above the rest of the wires forming the pile, thus permitting its being placed close to the heater-receiver. The resistance of this thermopile was about 7.9 ohms. The bismuth wire used was 0.06 mm diameter (length 4.5 mm) and the silver was 0.0308 mm diameter which explains the high resistance. The radiation sensitivity was up to the highest yet attained and the maximum deflection was attained in but a slightly greater time than (1.3 times) that of the galvanometer period. For example, using a galvanometer single swing of 3 seconds, the maximum deflection caused by warming the heater (whether heated electrically or heated by the absorption of radiant energy) occurred in less than 8 seconds. The radiation sensitivity was such that 1 microwatt of radiant energy produced about 0.19 microvolts or a rise in temperature of about 24×10^{-4} degree. The fourth thermopile constructed for

use in this instrument for making absolute measurements contained bismuth wire 0.1 mm in diameter and 45 mm in length. The elements were joined two in series-parallel as shown in illustration No. 1 of Fig. 3. Its sensitivity was the same (within 2 per cent, which is the normal variation for different thermopiles) as that of the instruments constructed of bismuth wire 3.5 mm in length. This is a further test to the one given on a previous page, showing that a length of 3.5 mm is sufficient to prevent a reduction in sensitivity by warming of the cold junction by heat conducted from the exposed junction.

The slit jaws were about 1 mm in front of the receiver and the thermopile was about 1.5 mm back of it. Gerlach's extensive tests show that the amount of overlapping of the receiver by the slit jaws does not affect the observations. Various electrical tests, e. g., reversing the current in the heater-receiver, showed that it was thoroughly insulated from the thermopile. Covering the opening in the slit jaws with a sheet of thick aluminum (bright and smoked) and exposing the instrument to intense radiation, showed no appreciable warming. This shows that in the short time that the instrument is exposed to radiation, the slit jaws are not sufficiently warmed to cause an appreciable radiation from them, upon the heater-receiver. When the whole receiver is exposed to radiation, these slit jaws are separated by a slightly greater amount than the width of the strip. The small amount of radiation which passes between the slit jaws and the edges of the receiver is absorbed by the smoked copper surfaces (K, Fig. 5) at the rear.

To prevent stray radiations from falling upon the receiver various arrangements of the slits and diaphragms were tried. One of these combinations tried was a slit S and a diaphragm S', as shown in Fig. 5A-A. In this arrangement the diaphragm S' is of copper 1 mm in thickness painted with lampblack and smoked on both sides. The slit S, of aluminum, 1.2 to 1.8 mm in thickness, is painted black, excepting a border about 5 mm wide, along the knife edge, which is highly polished. The four brass diaphragms (Fig. 5) and the inside of the brass tube which supports them are entirely covered with lampblack paint and smoked in the flame of sperm candle. In this manner most of the radia-

tions in the wide cone of rays emanating from the black body are absorbed at some distance from the receiver and hence there is but little chance for stray radiations to fall upon the receiver. The narrow, bright strip along the knife edge of the slit S absorbs but little radiation. The heat developed by absorption of radiation is speedily conducted away laterally from the knife edge. The shield S' is sufficiently heavy, so that (judging from the experience gained in a previous investigation of the diffuse reflecting power of lampblack) the temperature can not rise sufficiently to produce reradiation upon the receiver. In subsequent work this shield was placed upon the innermost diaphragm, D, which had an opening 3.3 cm in diameter, thus lessening the amount of diffuse radiation that might fall upon the receiver.

Attention has already been called to the fact that the "cold" deposits of soot from a sperm candle reflects diffusibly about 1.2 per cent. The diffuse reflecting power of soot, deposited by holding a cold metal plate in the tip of the flame of a sperm candle (or better still, an acetylene flame) is much lower in value, being of the order of 0.5 to 0.6 per cent.

From the foregoing description of the instrument as thus far developed, it may be seen that there is but little in common with Gerlach's device. The instrument is very sensitive, so that variation in the radiation from a black body caused by a variation of $0^{\circ}.1$ in temperature, at 800° to 900° C, was easily observed in the galvanometer deflections. Using a platinum receiver, the galvanometer deflection registers a maximum in 8 seconds. The instrument is easily and quickly operated, and hence if all the sources of stray radiations can be eliminated it promises to be an accurate pyrometer for refined temperature measurements. For this purpose it will be desirable to modify the instrument so that the various shields and diaphragms, W, may be water-cooled, as shown in Fig. 5E. In this design the thermopile, mounted as shown in Fig. 1G, is entirely inclosed and shielded from diffuse radiations.

The energy expended in heating the receiver is determined by measuring the drop in potential along the part of the strip exposed to radiation and the electric current through the strip. The current is determined by measuring the drop in potential across

a standard resistance of 1 ohm. When using a manganin or "therlo" receiver the resistance may be determined so that only the measurement of the current is necessary. The emfs are measured with a Leeds & Northrup type K potentiometer.

In view of the fact that this paper does not deal with the constants of total radiation, it will be sufficient to add that the numerical value of this constant as thus far observed with this type of radiometer is somewhat lower than Gerlach's value obtained with a somewhat similar instrument.

IX. SPECIAL DESIGNS OF THERMOPILES

Stellar thermoelements.^{22a}—A stellar radiometer differs from a laboratory instrument in that no shutter is required. Here the sky is the shutter and the observation consists in exposing the thermopile receiver alternately to a star and to the adjoining sky. Or, by exposing the two junctions alternately the deflections (in opposite directions) are doubled. In a refracting telescope the thermopile is shielded from nearby sky and water radiation, which is of wave lengths which are absorbed by the glass lenses. The zero reading therefore depends upon the temperature of the lenses forming the objective. In a reflector the thermopile (when in an inclosure having a fluorite or rock-salt window) radiates to the sky, and it is desirable to have the two junctions (receivers) of as nearly the same size and emissivity as is possible to construct them, in order to maintain symmetry. There is no apparent gain in using more than two junctions, because of the difficulty in maintaining symmetry and because of the difficulty of construction.

In the first experiments on thermopiles it was deemed desirable to use several elements in the receiver, and a thermopile was described which had 10 elements meeting at a point, with a receiver 1 mm in diameter. However, a star image is a mere point any way, hence, the receiver should be reduced to the smallest workable dimensions.

A high emf, small heat capacity, and symmetry of receivers are required. However, from the foregoing experiments it is evident that if the heat capacity of bismuth alloys can not be kept low, it is better to use the pure metal in spite of the fact that the

^{22a} See Appendix, Note 4.

thermoelectric power is 50 per cent lower. The sensitivity is increased from four to five times by placing the thermoelements in vacuum. The time to attain temperature equilibrium does not appear to be appreciably increased when the elements are in vacuum.

A further increase in the sensitivity is obtained by lengthening the period of the galvanometer.

Whether, under these conditions the point receiver thermopile can be made more sensitive than a bolometer, remains to be determined. In view of the fact that the heat conducted along the bolometer strip serves to change the resistance, while in the thermopile it is an impediment, it may be found in practice that the vacuum bolometer can be made more sensitive than the thermopile.^{22b}

Several stellar thermopiles were constructed, as shown in illustration No. 4 of Fig. 3, in which the receivers are 0.3 to 0.4 mm in diameter. The thermopile shown in Fig. 1F, having two elements in each receiver has not yet been tried. The distance between the two receivers is made 0.5 mm or less so as to facilitate exposing them alternately to a star image. Except by making an intercomparison against an arbitrary point source of radiation similar to a star image, there is no fair way of specifying the sensitivity, owing to the variable size of the receivers. It is hoped to compare the radiation from a star (e. g., Arcturus) with an artificial star and thereby establish a fair standard of comparison of this type of radiometer.

In the stellar thermopiles, as shown in Fig. 1F, and in No. 4, of Fig. 3, a short piece of bismuth wire 0.06 mm in diameter was pressed flat between two pieces of plate glass. The thickness was then 0.01 to 0.012 mm. This was then cut into narrow strips, perhaps 0.05 mm wide, by means of a sharp razor. These narrow strips were pressed to about 3 times their former width, and again cut into strips 0.03 mm to 0.07 mm in width. The estimated thickness was 0.005 mm. The silver wire used was 0.0165 mm in diameter. Fine globules (perhaps 0.03 to 0.05 mm in diameter) of tin were then attached to the silver wires and pressed to 0.3 to 0.4 mm diameter. The bismuth wire (about 2 mm long) was then

^{22b} However, in the preliminary tests, to be given in a forthcoming paper on stellar radiation measurements, the thermocouple was found more sensitive than the bolometer.

fused to this tin receiver. Wood's alloy was used to attach the silver wires to the binding posts. The receivers were painted with the previously described mixture of lampblack and platinum black, but not smoked. The resistance of such a thermoelement is from 2 to 2.8 ohms, depending upon the length of the bismuth wire. Elements were also constructed of bismuth alloys, of bismuth and platinum (Wollaston wire 0.005 to 0.01 mm in diameter) and of bismuth iron. They were mounted together in a receiver and tested under the same conditions. The bismuth-platinum element had a resistance of 5 to 6 ohms, half of which was contributed by the platinum. One bismuth-platinum thermoelement consisted of bismuth 1.9 mm in length and 0.071 mm in width. The platinum was 0.01 mm in diameter. The receivers of tin were respectively 0.29 and 0.33 mm in diameter. Its resistance was 4.58 ohms. It was more than twice as sensitive as the best bismuth silver ($\text{Ag} = 0.0165$ mm diameter) thermoelements of similar dimensions. This is owing to the fact that platinum has a much lower heat conductivity than silver. This thermoelement of bismuth-platinum, having a thermoelectric power of 80 to 85 microvolts, was found to be at least 25 per cent more sensitive than a similar thermoelement of bismuth, and an alloy of bismuth + 5 per cent tin which had a thermoelectric power of 127 microvolts. In the bismuth-bismuth alloy thermoelement the length of the bismuth was 2.2 mm, the width was 0.067 mm, and the resistance of the element was 11.55 ohms. The receivers were respectively 0.38 and 0.44 mm in diameter. Both elements were mounted in the same inclosure and tested against the same artificial star. The latter was a cylindrical acetylene flame with a pinhole opening in a diaphragm, which was placed in front of the flame. An image of this pinhole was projected upon the receiver. It is hoped to compare these with a vacuum bolometer of small heat capacity to determine the merits of these two types (bolometer and thermopile) of stellar radiometers. In such a test the bolometer and thermopile are to be mounted together in the same container. The evacuation of the air is produced by heating metallic calcium which is contained in a quartz tube.

An absolute thermopile for the measurement of nocturnal radiation.—On a previous page attention was called to the Ångström

pyrheliometer modified so as to reduce its heat capacity and hence render it quicker in its action by having the thermopile separated from the heater receiver. For the measurement of nocturnal radiation, which generally is a passage of radiation from the surface of the thermopile outward into space, a more massive heater receiver in contact with the thermopile is permissible, in order to minimize the effect of air currents.

The pyrheliometer of Ångström²⁴, as used for the measurement of nocturnal radiation, consists of two manganin strips, to each of which is attached a single thermoelement of iron and constantan. One strip is kept bright to prevent cooling by radiation. The other one is blackened to facilitate radiation, and hence undergoes the greatest changes in temperature, which is usually a cooling, since, on clear nights there is a passage of terrestrial radiation into space. An electric current is passed through this manganin strip to compensate for the cooling. From the resistance of the strip, the area, etc., the loss of radiation into space, may be determined in absolute measure.

In the present design, Fig. 1C, the thermoelements (Bi-0.1 mm; Ag-0.036 mm diameter. Receivers of tin 1.4 by 1.8 by 0.02 mm) are cemented directly to the four manganin strips, 0.033 mm in thickness and 2 mm in width, which are alternately black and bright. For the latter purpose the front surfaces are plated with a thin layer of gold. The reflecting power of lamp-black for long waves is about 3 per cent, and for gold it is about 97 per cent. The difference in the emissivities of these two surfaces should produce a far greater difference in temperature within the strips than is possible with a metallic surface having a lower reflecting power. For convenience in construction the thermoelements are in four rows, joined across the back of the mounting, as shown in the illustration. This part of the device was designed and constructed for the United States Weather Bureau for nocturnal radiation measurements. The instrument gave a maximum deflection in 15 seconds (galvanometer swing was 3 seconds) when exposed to a standard of radiation from which it appears that cementing the receivers directly in contact with the heavy man-

²⁴ K. Ångström: *Nova Acta Reg. Soc. Scient. Upsala* (4), 1, No. 2, 1905; A. Ångström: *Astrophys. J.*, 87, p. 305, 1913.

ganin strip does not seriously increase the heat capacity and hence the period of the instrument.

A thermopile for physiological problems.—An important problem in physiology is to determine definitely whether or not heat is evolved by a live nerve during tetanization. If there is a chemical reaction (oxidation of a carbohydrate in order to expedite a nervous wave) when the nerve is undergoing tetanus, either by an electrical or by a chemical stimulus, then there should be an evolution of heat with a consequent rise in temperature. The attempt was made by Hill ²⁸ to detect such a rise in temperature during the transmission of a nervous impulse by placing the exercised sciatic nerve of a frog upon the central row of thermo junctions (30 in number) of a Rubens iron-constantan thermopile. The receivers were small and hence could not make very effective contact with the nerve.

The proposition having been presented to design a bismuth-silver thermopile to meet the requirements of this problem, the modification illustrated in Fig. 1E was constructed. The device, which contains 20 thermo elements joined in series, was constructed of bismuth wire 0.1 mm in diameter, and silver wire 0.038 mm in diameter, the resistance being 9.45 ohms. The novelty in this thermopile consists in having the receivers bent into a U-shaped trough, 21.5 mm long and about 1.2 mm deep. The inside of each receiver was painted with lamp black and hence would acquire heat (if any be produced) by conduction and by radiation. For symmetry, samples of the material (nerve, muscle) under examination are placed in both troughs, and by exciting them alternately the galvanometer deflection (in opposite directions) will be doubled.

The sensitivity was tested by placing an insulated manganin wire 0.05 mm in diameter in the U-shaped receiver and passing through it an electric current of 0.001 ampere, which produced a large deflection (25 + cm) of the galvanometer. The test showed that using a galvanometer sensitivity of $i = 5 \times 10^{-10}$ ampere, a deflection of 1 mm = 3.8×10^{-8} watt = 9×10^{-8} g-cal. sec.⁻¹. The sensitivity was, of course, higher than this, for the wire heater did not lie closely throughout its whole length in contact with the receiver.

²⁸ Hill: J. Physiology, 42, p. 433; 1911.

In the hands of an experienced operator the galvanometer sensitivity could be increased 5 times, and reading to 0.2 mm it is safe to estimate that, with this device, an evolution of heat at the rate of 1×10^{-10} g-cal. sec.⁻¹ can be detected.

This thermopile behaved exactly as the others with flat receivers. It was entirely free from drift and produced a maximum deflection in $4/3$ the free swing of the galvanometer. As an ammeter this device should be useful for certain classes of measurements of electrical currents. In the latter application, however, the heater would no doubt be more efficient in the form of a flat strip as used in the thermopile for absolute measurements described on another page.

The thermopile as a photometer.—The requirement of this thermopile was to measure the blackening produced by star images on photographic plates. These star images were to be magnified and projected upon the thermopile receiver which was to be a disk 5 mm in diameter. The first design was constructed as shown in illustration No. 4 of Fig. 3. The receivers were semicircular disks (of tin 0.02 mm in thickness) to each of which were attached two thermoelements of bismuth (0.1 mm) and silver. This series-parallel arrangement had a resistance of 1.2 ohms; and it required 10 to 12 seconds to attain temperature equilibrium. Blackening the rear side of the receivers (in order to increase the emissivity) decreased this period only about 1 second. From other experiments it was concluded that this lag in attaining temperature equilibrium was owing to the slowness of heat conductivity from the extreme edges of the disk, distant from 2 to 2.5 mm. Another thermopile was therefore constructed of exactly similar material, the only modification in the design being in the receiver, which was cut into four quadrants. One thermoelement was attached to the center of each quadrant, and the four elements joined in series as shown in illustrations No. 3 of Fig. 3, and in Fig. 1B. The resistance was 2.4 ohms. This receiver, when exposed to radiation, attained temperature equilibrium in 5 seconds. Its radiation sensitivity was the highest of all the instruments constructed, being 39 per square millimeter area against 33, which is the average value on the (arbitrary) scale of comparison. The area exposed is closely the same as that of the linear thermopiles, herein described, and

its high sensitivity appears to be due to the fact that this area is comprised within a circle, which arrangement is the most efficient construction of a thermopile receiver.

A thermoelement with a concentrating mirror.—The loss in efficiency in a large receiver is so great that in some kinds of work it may be more advantageous to use a small receiver and concentrate the radiations not intercepted by it upon the rear side of the receiver by means of a cylindrical mirror or by means of a cylindrical lens in front of the receiver. For example, the sensitivity of a receiver (16 mm long) which is used to measure the intensity of the radiation in a spectral line 1 mm wide and 16 mm long is only four times as great as that of a receiver 1 mm long. If, for the measurement of the energy in a spectral line 16 mm long (and 1 mm wide), we place a concave cylindrical mirror at the rear of a receiver 1 mm long (and 1 mm wide), thus concentrating upon the receiver the energy not intercepted by it, we obtain the integrated effect of practically 16 receivers, each one of which is 1 mm in length, and the galvanometer deflection will be about four times that observed when using a receiver 16 mm long. As shown in Fig. 6, one receiver gave a deflection of over 40 cm, four receivers gave a deflection of 80 cm, while 18 receivers gave a deflection of only 180 cm instead of about 700 cm, which would have been obtained if the energy could have been concentrated upon the single receiver.

A hole in the center of the mirror permits adjusting the position of the thermopile in the spectrum (as described in Part VII of this paper). Using the finest material that can be manipulated (as described in the first caption of Part IX) in a highly exhausted inclosure, a single element and concentrating mirror should prove useful in some special kinds of radiometry, requiring the highest attainable sensitivity. For routine work, however, the regular linear thermopile in air is preferable.

Miscellaneous designs.—Under this heading may be mentioned designs of thermopiles which have already been constructed and tested; and also suggested improvements in others. For receivers in radiotelegraphy two forms were constructed which were kindly tested by Dr. L. W. Austin. The one consisted of strip of bolometer platinum 1 mm wide, about 15 mm long (resistance, 4 ohms),

insulated between two thermopiles of bismuth and silver. The bismuth wires were 0.06 mm in diameter, pressed flat. The 0.03 mm silver wires were attached to these flat strips of bismuth, but no receivers were used. Either the platinum heater or the thermopile could be placed in the radio-receiving circuit. The device was reported to be very sensitive; but it was defective in that the platinum heater became warmed, causing a shift of the zero reading of the galvanometer. The second thermopile consisted of 0.06 mm bismuth wire and 0.03 mm silver wire, in which a mass of Wood's alloy was fused to the alternate junctures (and blackened), in order to change the heat capacity, so that the smaller junctures would become the more highly heated by the oscillating electric current passing through the instrument, and thus produce a thermoelectric current. The instrument was reported to be about as sensitive as a special tellurium couple in regular use. Since there did not appear to be a very marked gain in sensitivity as compared with other devices already in use, no further attempts were made in applying this thermopile in radiotelegraphy.

Another device, in the form of a thermoelectric generator capable of generating current by exposing it to sunlight deserves further attention experimentally. In it bismuth and copper, or copper and constantan thermoelements, with large receiving surfaces attached thereto may be used. The receiving surfaces are covered with asphaltum and the whole is inclosed in a glass covered box.³⁶ The coronal thermopile constructed by Callendar³⁷ is an ingenious device consisting of bars of bismuth and antimony, with receiving surfaces in the form of copper rectangles. The receivers, which are arranged in the form of an annulus, are mounted in the eyepiece of a telescope and sighted at the moon during a solar eclipse. It appears possible to produce a quicker acting and perhaps a more sensitive instrument (radiometrically) by using a thermopile of bismuth silver with the tin receivers cut into the form of an annulus. For measuring the radiation from the solar corona Julius used a thermopile with a receiving disk 5 mm in diameter. Instead of the annulus, the disk receiver shown

³⁶ For a further description, see Letters Patent No. 1 077 210, Oct. 28, 1913, which is dedicated to the public.

³⁷ Callendar: *Proc. Roy. Soc.*, 77A, p. 8; 1905.

in illustration No. 3 of Fig. 3 might be useful. If desired, the central portion could be covered with a smaller disk leaving an annulus of the required size.

As an illustration of the wide range of usefulness of the thermopile, it may be added that an instrument was constructed in which the receiver was in the form of a U-shaped trough, within or over which was suspended a wire through which a heavy electric current could be passed. The device is to be used as an ammeter, and its use was invoked to avoid distortion of the form of the electric wave used in a delicate magnetic test.

The thermogalvanometers on the market are said to be slow in their action. The fine bismuth wires now attainable, combined with a disk built up of quadrants as shown in No. 3 of Fig. 3, would produce a quick acting and perhaps a more sensitive instrument.

X. SPECIFICATION OF THE RADIATION SENSITIVITY OF A THERMOPILE

From the foregoing experiments it is evident that the radiation sensitivity of a thermopile can not always be defined in terms of the voltage produced. "Microvolts per microwatt" of radiant energy absorbed has but little meaning when used in connection with a Thomson galvanometer. This definition of sensitivity is, of course, useful when the measurements are made with a potentiometer or with a moving coil galvanometer. The (Thomson) galvanometer deflection was found the same for two thermopiles having the same area exposed; the one having its 18 elements in series, the other having its 18 elements joined two in series-parallel thus producing only half the voltage of the former. In the latter the heat capacity and emissivity was so far reduced that 1 microwatt of radiant energy produced 0.016 microvolt (or greater) per thermal junction. Since the thermoelectric power of bismuth silver is about 80 microvolts per degree, this is equivalent to a rise in temperature of about 20×10^{-5} degree. In the herein described thermopile of bismuth alloy, the temperature rise was of the order of 26×10^{-5} degree, while in the circular receiver, illustration No. 3 of Fig. 3, the temperature rise was 46×10^{-5} degree (or even higher according to the direct measurement of the voltage) per microwatt of radiant energy absorbed. While

this description of the rise in temperature of the receiver shows the efficiency of these designs it is not so convenient as the time-worn specification of sensitivity in terms of the current sensitivity of the galvanometer, and a standard of radiation. However, instead of using the candle as a source of radiation, a calibrated incandescent lamp is recommended.²⁸ The current sensitivity of the galvanometer may be taken as 1 mm deflection = 1×10^{-10} ampere. With this galvanometer sensitivity, 1 microwatt of radiant energy produces a deflection of x -centimeters per square millimeter of the receiver which is exposed to radiation. As a further check, the total area exposed and the scale distance (1 meter) should also be specified.

The specification of the area exposed is desirable in view of the fact that the sensitivity is proportional to the square root of the total area exposed. This was thoroughly demonstrated on the large thermopile shown in illustration No. 2 of Fig. 3, the individual receivers of which were 1.5 by 3 mm (=4.5 mm²) in area. Additional terminals were soldered to the small metal posts which support the individual elements, as described in the fore part of this paper. In this manner it was possible to determine the sensitivity of 4, 6, 8, 10, or 18 junctions. The observed galvanometer deflections had to be corrected, of course, for variation in external resistance, by means of the data given in Fig. 2. The total area exposed was taken to be 4.5 mm² times the number of junctions used. The galvanometer sensitivity and the standard of radiation were, of course, kept constant. The intensity of the radiation was 83×10^{-8} watt per mm². The results obtained are given in Fig. 6, in which the ordinates are the observed galvanometer deflections in centimeters and the abscissae are the square roots of the areas exposed to radiation. The data are in exact agreement with the square root law as applied to a large receiving surface containing a plurality of thermojunctions. The data are in apparent disagreement with the results published in a previous paper²⁹, which, however, relate to different conditions of the receiver. In the previous paper the experiments relate to a single thermoelement attached to a single receiver, the area of which was varied. It was then found, as was to be expected,

²⁸ This Bulletin, 11, p. 87, 1914; J. Franklin Inst., 176, p. 219; 1913.

²⁹ This Bulletin, 9, p. 7; 1912.

that there is an optimum size of receiver giving a sensitivity which is considerably (30 to 50 per cent) higher than the values obtained by applying the square root law, to observations on very small or very large receivers. From this it is evident that the best thermopile is obtained by using the most favorable area in the individual receivers.

In previous papers the sensitivities of the various types of radiometers were intercompared by considering the sensitivity proportional to the area. The sensitivity per square millimeter area exposed was therefore obtained by dividing the total deflection

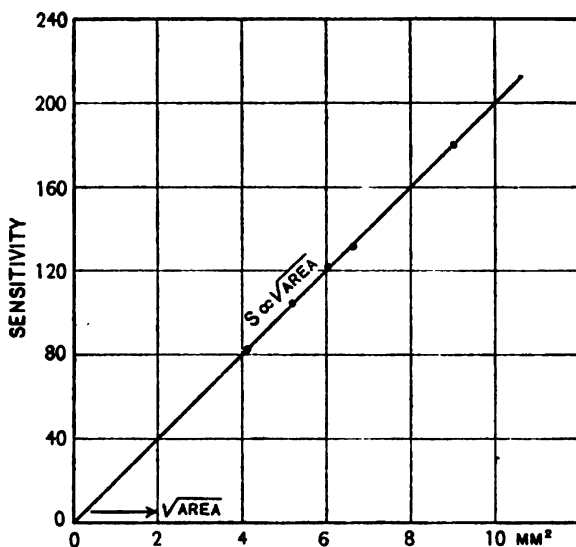


FIG. 6

(the radiometer was exposed to a standard candle) by the total area exposed. It was, of course, realized that the comparison was not a fair one; but it was in keeping with the accuracy of the data published by various experimenters. For bolometers and thermopiles the square root of the total area exposed should be used as the divisor. On this basis of comparison the average radiation sensitivity of the bismuth-silver thermopiles herein described was such that 1 microwatt of radiant energy produced a deflection of 2.9 to 3.0 cm per mm² area exposed; scale at 1 meter; galvanometer sensitivity $i = 1 \times 10^{-10}$ ampere. For example,

thermopile No. 36 (having two elements in series-parallel; resistance 1.98 ohms; area exposed 31.2 mm^2 ; $\sqrt{\text{area}} = 5.58$) produced a deflection of 97.5 cm for a galvanometer sensitivity of $i = 4.1 \times 10^{-10}$ ampere. This deflection must be corrected by 9 per cent for inequality of external resistance (see Fig. 2) and by 1.5 per cent for the energy lost by reflection from the lampblack surface of the receiver. This corrected value (which is 107.7 cm) when reduced to the value which would be observed with a galvanometer sensitivity of $i = 1 \times 10^{-10}$ ampere, is equivalent to a deflection of about 445 cm. The intensity of the radiation from the standard lamp being 88.9×10^{-8} watt per mm^2 , the total radiation falling upon the thermopile was (the total area exposed, $31.2 \times 88.9 =$) 27.7×10^{-6} watt. Hence 1 microwatt of radiant energy produced a deflection of $(445 \div 27.7 =)$ 16.1 cm and the sensitivity in centimeters deflection per mm^2 of the total area exposed was $(16.1 \div 5.58 =)$ 2.89 cm.

On the old basis of comparison, against a sperm candle which has a radiation intensity of about 30 microwatts per mm^2 , at a distance of 1 meter from the flame, the radiation sensitivity of these thermopiles is of the order of 87 to 90 cm per mm^2 of the receiver exposed to radiation. Some of the special designs of bismuth and silver had a 15 to 20 per cent higher sensitivity. However, the values just quoted are conservative estimates of what may be attained without serious difficulties in construction.

XI. SUMMARY

The novelty of the bismuth-silver thermopile⁴⁰ as herein described consists of a receiver having a continuous surface and a definite area which permits calibration, for measurements in absolute measure.

Data are given on the relative sensitivities of thermopiles of bismuth silver, bismuth copper, bismuth alloys, and of bismuth iron. It is shown that the attainment of a high radiation sensitivity in a thermopile is mainly a question of neatness of construction (low heat capacity, conductivity, and emissivity) and that the thermoelectric power is of secondary importance. The radiation sensitivity of a thermopile of bismuth and silver is

⁴⁰ For further specifications, see Letters Patent, 1 081 365, Dec. 16, 1913; dedicated to the public.

almost (within 10 per cent) as high as that of a thermopile of bismuth alloy having a 55 per cent higher thermoelectric power. These thermopiles have practically the same radiation sensitivity as a good air bolometer, and they are not so easily disturbed by air currents. They embody practically all the good qualities (except instantaneousness of action) of the bolometer.

Experiments are described on the radiation sensitivity of a thermopile as a function of the area exposed, and of the thermoconductivity and emissivity; also as a function of the external and the internal resistance. It is shown that the external (galvanometer) resistance may be two or three times the internal resistance without decreasing the sensitivity more than 5 or 10 per cent. After correcting for the difference in internal and external resistance, it was found that the radiation sensitivity of the thermopiles having all the elements in series was nearly as high as that of the thermopiles having the elements joined two in series-parallel.

A radiometer attachment to monochromatic illuminators is described, which enables the operator quickly and easily to determine the energy value of the stimulus. This is of importance to physiologists, psychologists, biologists and physicists who are investigating the effect of light stimuli upon matter.

A thermopile with a thin blackened strip of manganin or platinum in front of it, is described. This is a modification of the Ångström pyrheliometer, and it affords a quick and an accurate method for the measurement of radiant energy in absolute measure.

Special designs of thermopiles are described. They include stellar thermopiles; thermopiles for measuring nocturnal radiation; thermopiles to be used as photometers; thermopiles with the receivers in the form of U-shaped troughs for physiological problems; and miscellaneous thermopiles for measuring small electric currents in radiotelegraphy, etc.

The results herein described are part of the experience gained in the construction of various designs and modifications of thermopiles to suit various problems which promised solution by radiometric methods. It has involved the construction of more than 1000 thermal elements and (since each element consists of 5

pieces) the handling of about 5000 or more pieces of material. The failures are of course not described. After several days of work on a new design the resulting thermopiles sometimes proved less valuable than the frame upon which it was mounted. It was therefore promptly cut from the frame, to be replaced after four hours further work with a similar design having the properties herein described. This was the experience with the very first thermopile (of bismuth iron) which led to the construction of the first bismuth-silver thermopile; and it was the experience of the first series-parallel arrangement of the elements. The data are given with the hope that they may be of assistance to others in widening the field of usefulness of this form of radiometer.

In conclusion it is pertinent to add that the thermopile and the bolometer recognize no sharp dividing line of "ultra-violet," "visible," and "infra-red" as marked by the eye and the selenium cell. Using a suitable spectrometer it is just as easy to observe in the ultra-violet as in the extreme infra-red. Using the spark spectra of Al, Mg, Cd, and Zn; the acetylene flame; the nitrogen-filled tungsten lamp; or the Nernst glower, much valuable work may be done throughout the spectrum, extending to 0.25μ or to even shorter wave lengths in the ultra-violet. The thermopile therefore deserves a fair trial as compared with the spectrophotometer, which is limited in range, and as compared with photographic photometry with its questionable time exposure, fogging of plates in development, and standardization of plates, which vary in sensitivity in different parts of the spectrum.

WASHINGTON, March 20, 1914.

APPENDIX

NOTE 1.—GALVANOMETER MIRRORS

The idea seems to prevail that thin glass or quartz mirrors with plane surfaces can not be made plane or kept plane in mounting them; and hence selected microscope cover glass will be just as satisfactory. This is entirely erroneous, for the surface of the thin cover glass is extremely uneven. On the other hand the optically worked material of the same thickness as the cover glass is free from unevenness over its surface. In mounting such a thin mirror the surface may become curved (this is also true of the cover glass), but it will have a definite curvature without the minor undulations to be found in the cover glass.

Having had such optically worked mirrors in successful use for several years, it is desirable to call attention to their superior qualities, as well as the manner of construction. The first step in producing these thin mirrors is to grind a flat surface upon a thick (5 to 8 mm) plate of glass which acts as a holder. The sample which is to be used for mirrors is also ground flat, and polished on one side, which is then cemented to the glass holder. The other side of the sample is then ground flat. The sample may be wedge shaped but that is unimportant. Having ground the sample to the desired thickness (say 0.08 mm to 0.15) the surface is polished, and it may be rendered optically plane to one-fourth of a wave length of light. On removing this thin plate from the holder it will be found that the surfaces are plane to one-fourth (to one-half) of a wave length of light. This plate is then platinized by cathode disintegration and cut into strips of the desired dimensions by means of a crystal of carborundum. Mirrors produced by cathode disintegration of antimony are white and usually more highly reflecting, which suggests the use of this metal, since platinum is inclined to produce brownish colored mirrors. The mirror is attached to the galvanometer suspension by a mere trace of adhesive material, e. g., universal wax or tallow, and there is no tendency to distort the mirror which happens when it is attached with shellac. The weight of such a mirror, 2.5 by 1.5 by 0.1 mm is about 1.5 mg.

NOTE 2.—VACUUM GALVANOMETERS

The current sensitivity of a needle galvanometer is usually stated to be proportional to the square of the period; and it is also proportional to the square root of the resistance of the coils.⁴¹

⁴¹ Kohlrausch Lehrbuch Praktischen Physik. Jaeger., Ann. der Phys. (4), 21, p. 63; 1906.

This may have been true of the older forms of galvanometers with their ponderous magnet systems, but the sensitivity of the galvanometers of recent construction, with their light suspended systems, is not proportional to the square of the period. In a paper by Abbott⁴² attention was called to this fact. With reference to the suspensions used by him no definite statement was made as to their behavior other than that "the deflection is not even approximately proportional to the square of the period." However, by exhausting the air to 0.2 mm pressure, he found that "the deflection was proportional to the square of the time of swing up to a time of single swing of 5.5 seconds." If this refers to the 16-coil galvanometer, it may explain the discrepancy between his observation and those by the writer.

In a previous paper⁴³ data were published showing that the sensitivity of the 4-coil galvanometers used by the writer is proportional to the period. It was therefore of interest to try one of these galvanometers in vacuo. For this purpose the four 26-ohm coils (mentioned on a previous page), mounted in Swedish iron shields, was used. A glass bell jar was placed over it and the air was exhausted to less than 0.1 mm.

The coils were wound in 5 layers of about 5 ohms each of Nos. 40, 38, 36, 34, and 28, B. S. gauge wire covered with a single layer of white silk. The outer diameter was 33 mm. The magnet suspension consisted of two groups of magnets, having 4 needles in each group. These needles were from 1.2 to 1.5 mm long (longer than usual) and the total weight was about 6 mg, the mirror weighing 1.5 mg.

The sensitivity test in air showed that the law of current sensitivity with square root of the resistance held for the series-parallel (26 ohms) and all in parallel (6.5 ohms), but fell below the required value by 8 per cent for all coils in series (104 ohms). This galvanometer was not constructed with the expectation of surpassing others on hand. The suspension and especially the mirror was heavier than is usually employed. The main interest in this test was its behavior in vacuum, to be described.

The results of this test show (see Fig. 7, the circles represent an entirely new set up of the instrument) that for a single swing greater than two seconds, the sensitivity, in air, is proportional to the time of swing, while in vacuum the sensitivity increased somewhat more rapidly than the time of swing. The actual gain in sensitivity in a vacuum was about 100 per cent for a swing of two seconds, and only about 25 per cent when the swing was greater than four seconds. In air, with a single swing of four

⁴² Abbott: *Astrophys. J.*, 18, p. 1; 1903.

⁴³ This Bulletin, 9, p. 7; 1912.

seconds, the deflection was completely damped; and with the air exhausted the needle had one turning point of small amplitude before coming to rest. For a time of single swing of two seconds the needle had two turning points before coming to rest, but in air the amplitude of swing was much less. The damping is evidently almost entirely magnetic, but it is not sufficient to be affected by the external resistance. In fact the writer has had but

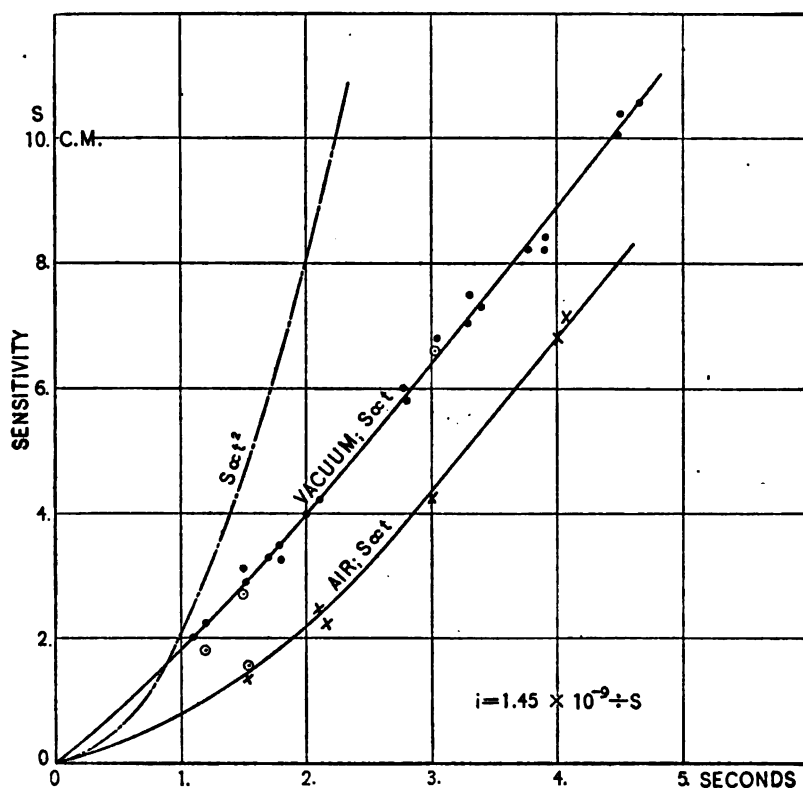


FIG. 7

one Thomson galvanometer in which the damping was affected by the external resistance in circuit. The magnets in the present galvanometer suspension were made from fine piano wire, hammered flat and hardened "glass hard." From the results obtained it appears that one must test the galvanometer before being certain that there will be a marked gain by placing it in an evacuated inclosure.

The iron clad galvanometer previously described⁴⁴ has been found to possess such excellent magnetic shielding that a more elaborate one was constructed. It is shown in Fig. 8. The four coils are embedded in blocks of Swedish iron, each block being 2.5 by 5 by 9 cm. Theoretically a circular form would be better because it is more symmetrical. A lamellated shield is shown in the right-hand side of the illustration. It consists of about 15 turns of transformer iron 0.4 mm in thickness. It is of course unnecessary to have the slots cut in the shield, especially the one at the bottom. This combination provides almost as good magnetic shielding as the more elaborate soft pipe outfit previously described. There are of course additional shields provided.

NOTE 3.—THE MOST EFFICIENT COMBINATION OF THERMOPILE AND GALVANOMETER RESISTANCE

In the foregoing tests of the sensitivity of thermopiles the same galvanometer was used. After making a correction for loss in efficiency due to inequality of internal and external resistance, it was found that the sensitivity of the type of thermopile having all the elements in series (resistance about 8 ohms) was practically the same as that of the type of thermopile having two elements joined in series-parallel (resistance about 2 ohms). Hence, aside from the fact that the series-parallel arrangement may be the quicker in attaining temperature equilibrium, there is no preference in the manner of construction of the thermopile when using a Thomson galvanometer. However, in the fulfillment of the condition of equality of internal and external resistance, a question remaining unanswered is the most efficient resistance of galvanometer coils to be used with the thermopile, i. e., whether a galvanometer made of coils of high resistance (say 4 coils each having a resistance of 32 ohms, and all in parallel giving 8 ohms) should be used with the thermopile of 8 ohms, or whether a galvanometer having coils of low resistance (4 coils in parallel, each coil having a resistance of 8 ohms) should be used with this same thermopile, having its elements joined two in series-parallel, and thus having a resistance of about 2 ohms. Another combination would be four coils of 2 ohms each joined in series-parallel. Theoretically, the force exerted by a coil varies nearly proportionally to the square root of the resistance. While this relation does not hold for large resistances, the results⁴⁵ shown in Fig. 9, indicate that a galvanometer having four coils of 32 ohms each (and giving 8 ohms when joined in parallel) is 6 per cent less sensitive than

⁴⁴ This Bulletin, 9, p. 61; 1912 (see Fig. 17).

⁴⁵ This curve is computed from data published by Abbott (*Annals Astrophys. Obs.*, 1, p. 250) on the force exerted by galvanometer coils of different resistances.



FIG. 8.—*Ironclad galvanometer*

a galvanometer having four coils of 8 ohms each, or 2 ohms when all the coils are joined in parallel. This is not a very marked difference in sensitivity, and as with the various thermopiles constructed, the writer's experience is that the sensitivity attainable in a galvanometer is dependent mainly upon the construction of the suspended system.

The radiation sensitivity of a bismuth-silver thermopile with 16 elements joined two in series-parallel and having a resistance of 1.84 ohms, was tested when connected with galvanometer coils differing widely in resistance. The first galvanometer which was used was constructed of coils having a resistance of 21 ohms (B. S. No. 40, 34, and 28 wire), and as used, with all the coils in parallel, had a resistance of 5.09 ohms. From the experiments on external and internal resistance, a correction of about 10 per cent had to

be applied to the deflections when using this thermopile. The second galvanometer was constructed of four coils, each having a resistance of 7.6 ohms (B. S. No. 38, 30, and 26 wire), and as used had a resistance of 1.92 ohms. The computed normal current sensitivity⁴⁶ appeared to be very closely the same for these two instruments.

These two galvanometers were used with the same thermopile of 1.9 ohms, corrections being made for inequality of external resistance when using the one galvanometer. The thermopile was exposed to a standard of radiation. The deflections were considerably larger (10 to 15 per cent) when using the low-resistance galvanometer. The efficiency (in galvanometer deflections) of the low-resistance combination appeared to be 10 to 15 per cent higher than was to be expected from the high-resistance combination. In other words, the low-resistance thermopile (elements joined in series-parallel) and an equally

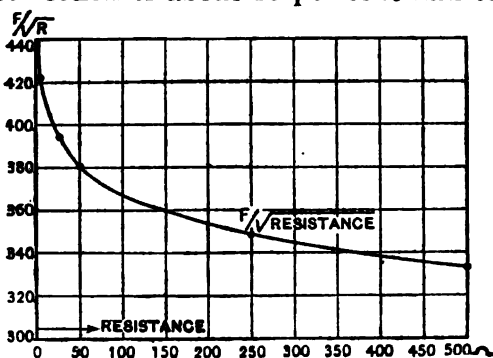


FIG. 9

⁴⁶ The normal sensitivity is usually defined to be the deflection produced at a distance of 1 m when a current of 1×10^{-8} amperes is passed through the galvanometer, the time of complete swing being brought up to 10 seconds and the resistance being reduced to 1 ohm. For this purpose the sensitivity is usually taken to be proportional to the square of the period and proportional to the square root of the resistance. The procedure is misleading, especially as regards the period. In some of the galvanometers described by various experimenters, the mirror is so small that the scale can not be placed at a much greater distance than 1 m. Moreover, the coils (15 to 20 mm in diameter) do not give a large range of proportionality of deflections with current. In the present galvanometers the coils are 33 mm in diameter; they have a large range of proportionality of deflection (50 cm) with current, and the sensitivity may be increased by lengthening the scale distance of 3 m. The sensitivity is proportional to the period, at least for periods greater than 1 second, which is the usual condition of operation.

low-resistance Thomson galvanometer seem preferable to the high-resistance (elements all in series) thermopile and its auxiliary galvanometer.

On the other hand, if the thermopile is used with a d'Arsonval galvanometer, conditions are different, owing to the large (external) critical damping resistance in this instrument. As already mentioned, it is desirable to use a great many thermoelements joined all in series when the thermopile is to be used with a moving coil galvanometer. In this manner the greater part of the critical damping resistance of the galvanometer may be replaced by the resistance of the thermopile. For example, a critical damping resistance of 10 to 12 ohms may easily be supplied by a thermopile of 20 to 24 thermoelements, which are joined in series. The emf produced will be twice that of the elements joined two in series-parallel, and the galvanometer deflection of the all-in-series arrangement should be twice that of the two-in-series-parallel arrangement. This, of course, is just the opposite to the results with the Thomson galvanometer. The latter, however, is the more sensitive instrument, and on a single swing of 2 to 3 seconds a current sensitivity of $i = 3$ by 10^{-10} amperes is easily attained.

NOTE 4.—TEST OF STELLAR THERMOELEMENTS ON STARS

While this paper was in press it was possible, through the courtesy of Dr. W. W. Campbell, Director of Lick Observatory, to test the sensitivity of some of the stellar thermoelements, just described in connection with the Crossley reflector. For this purpose from two to three elements were mounted in evacuated glass receptacles, as shown in Fig. 10, which contains two elements. Instead of the fiber mounting shown in Fig. 3, No. 4, the elements were attached to platinum lead wires, which were sealed into a glass tube. To the platinum wires were attached copper wires, No. 1 and No. 2, shown in Fig. 10. The glass tube containing the platinum wires was sealed into a thick piece of plate glass, G, by means of Khotinsky cement, K. The quartz-glass tube, containing the metallic calcium, Ca, was likewise attached permanently with this cement, K. The main portion of this glass receptacle consisted of a single piece of glass, E, with a projecting glass tube containing potential terminals, P, for testing the evacuation. A fluorite window, F, admitted the stellar radiations into this glass vessel, and upon the thermoelements, which are supported by the platinum lead wires to be seen through the glass vessel E. The rear window of glass G was attached by means of stopcock grease, covered with Chatterton wax.

This peculiar form of construction was necessary in order to be able to use the device when attached to the plate holder, in the

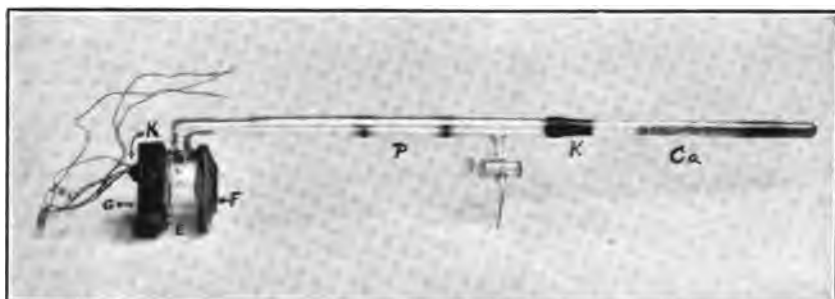


FIG. 10

focus of the telescope mirror. The star image and the receivers of the thermoelement are viewed from the side of the telescope tube by means of a right-angled prism and a lens mounted close to the glass plate G. It was therefore necessary to design the radiometric attachment so that all projecting parts extended downward in the direction of the reflecting mirror. This mirror has a focal length of 534 cm and a clear aperture of 92 cm, affording a ratio of aperture to focal length of 1 to 5.8.

Two receptacles, as shown in Fig. 10, were prepared for the test. The one (No. 7) contained an element of bismuth-platinum and an element of bismuth-bismuth tin alloy (5 per cent tin). The second receptacle (No. 6) contained an element of bismuth-bismuth and tin alloy, and two elements of bismuth-platinum. In one of the latter elements the bismuth was folded so that the two receivers were side by side, in order to easily expose the receivers alternately to the star image. The two elements in receptacle No. 7 were selected from the best found in previous tests and were remounted. The three elements in receptacle No. 6 were mounted just before leaving for Mount Hamilton, and there was no time for the preliminary radiation sensitivity tests.

These two receptacles were evacuated, the stopcocks were secured with Chatterton compound, and the vacuum was thereafter maintained by warming the metallic calcium, Ca, Fig. 10, by means of a small alcohol blast lamp. This outfit was taken to Mount Hamilton, Cal., a distance of about 3200 miles, without serious mishap (one element in No. 6 was broken in climbing the mountain), and the calcium was occasionally heated with the alcohol blast lamp to remove any vapors that may have been evolved. Some time after arrival on Mount Hamilton one of the receptacles began to leak a little. This was remedied by applying a coat of shellac to the ground joints. A vacuum pump was taken along for security against serious accidents, but it was never unpacked. From this it is evident that, equipped with a number of evacuated receptacles containing thermoelements, one can go to the remotest regions to make radiometric measurements without being obliged to carry a heavy pump. This is one of the principal achievements in connection with the work.

In the radiation sensitivity tests on stars it was found, as it had been previously observed in the tests on artificial stars, that there was but little difference in the radiation sensitivity of bismuth-platinum thermoelements as compared with the elements of bismuth-bismuth and tin alloy which had a 50 per cent greater thermoelectric power. The pair of elements used in No. 7 were selected from previous tests, and, as used in the reflector, the element of bismuth-bismuth and tin alloy was only about 10 per cent more

sensitive than the element of bismuth-platinum. In the latter the receivers were tin globules pressed flat, as already described. In the former the receivers were of Wood's alloy (used as a solder), which was pressed into a thin disk between thin plates of mica, the pressure being applied when the solder was in a molten state.

The behavior of the bismuth-bismuth tin alloy element in receptacle No. 6 was unusual in that one receiver (of Wood's alloy pressed flat when in a molten state) was about 40 per cent more sensitive than the other. The least sensitive receiver attached to this element was about 10 per cent less sensitive than the receivers joined to the element of bismuth-platinum. In the latter the two receivers had practically the same radiation sensitivity.

It is beyond the scope of the present paper to include the results obtained in measuring the radiation from stars. These radiation measurements are quantitative on stars down to the 5.3 magnitude, while good qualitative measurements were made on stars down to the 6.6 magnitude. In all, 112 celestial objects were measured, including Saturn's rings, the dark and the bright belts of Jupiter (also a pair of his moons which happened to be close together), and a planetary nebula, which, however, gave no positive deflections. In this preliminary survey it was shown that red stars are emitting radiation at a far more rapid rate than blue stars of the same photometric magnitude. These observations were substantiated by using an absorption cell of water 1 cm in thickness, which absorbs all the infra-red beyond $1.4\ \mu$. This test eliminated the question of the size and the distance of the star. It showed that comparing stars of the same photometric brightness, the red stars emit from 2 to 3 times as much infra-red radiation as do the yellow and the blue stars. This shows why it is that a red star causes a galvanometer deflection which is 2 to 3 times that produced by a blue star of the same photometric brightness.

Before going to Mount Hamilton it was the intention to use certain stars as standards of radiation in testing the radiation sensitivity of the thermocouples. After several nights of observation it was found that a slight variation in humidity caused a great variation in the total amount of radiation from the standard star, so that any possible variation in the radiation sensitivity of the thermocouple was negligible in making the measurements. In other words, the thermocouple was used to observe the variation of atmospheric transparency for stellar radiations. This variation in transparency was most marked for red stars, as was to be expected from the tests with the water cell.

Time did not permit the construction and testing of stellar bolometers, as had been planned, to compare with the stellar thermopiles. However, from tests made in the laboratory and from the tests of vacuum bolometers by Buchwald,⁴⁷ it does not appear that the radiation sensitivity of a vacuum bolometer will be much higher than the radiation sensitivity of the herein-described vacuum thermoelements. Buchwald's experiments show that the radiation sensitivity of the bolometer was increased from 4 to 5 times when the air was evacuated to a pressure of 0.001 mm, which is the same increase in sensitivity as observed in the herein-described thermoelements. The thermoelement is no doubt the least affected by wind and by temperature variations, so that, even though it may be slightly less sensitive than the bolometer, it will be the steadier in its behavior when connected with the auxiliary galvanometer, and it will be possible to read smaller deflections. On several nights observations were made on stars with a wind blowing upon the apparatus at a velocity of over 20 miles per hour, which gives some idea of the steadiness of the stellar thermocouple.

It is of interest to record that the galvanometer used in these tests was the ironclad instrument shown in Fig. 8. It stood upon the south pier which forms one of the two supports of the polar axis of the reflector. The galvanometer was therefore very close to the heavy iron telescope tube. In spite of this fact, the rotation of the telescope tube affected the galvanometer only when the reflector was directed upon stars situated low on the northern horizon, which brought the lower end of the telescope tube within 1 meter from the galvanometer.

It is of interest to record also that aside from its excellent magnetic shielding the galvanometer sensitivity was not greater than that ordinarily used in the Bureau of Standards, viz, $i = 1.5 \times 10^{-10}$ ampere.

NOTE 5.—THE MAINTENANCE OF HIGH VACUA BY MEANS OF METALLIC CALCIUM

It is a well-known fact that metallic calcium when heated has the property of combining with all atmospheric gases except argon. The application of this property of metallic calcium as an evacuator has been suggested as a result of the researches made by Moissan⁴⁸ and by Arndt.⁴⁹ Experiments on the production of high vacua by means of metallic calcium have been made by

⁴⁷ Buchwald: *Ann. der Phys.* (4), 85, p. 928, 1910.

⁴⁸ Moissan: *Compt. Rend.*, 127, p. 29, 497, 584; 129, p. 1757, 1898.

⁴⁹ Arndt: *Ber. d. Deutsch. Chem. Gesell.*, 37, p. 4733; 1904.

Soddy.⁵⁰ A summary of the results of these experiments may be found in Baly's *Spectroscopy*.⁵¹

In preparing the receptacles for the thermoelements shown in Fig. 10 the main difficulty experienced was in producing an air-tight container. This required so much time that, starting with the general information that calcium is useful in producing a vacuum, the application of this material for maintaining a vacuum in the present apparatus was perfected independently of previous work. In fact, the paper by Soddy was not consulted until after arrival on Mount Hamilton. This no doubt was a fortunate procedure, for some of the results obtained in the use of calcium as an evacuator seem to be at variance with previous experiments and also at variance with the prevailing notion that calcium very readily attacks quartz. For example, it was found that a light-walled, quartz-glass tube could be used to contain the metallic calcium, as shown in Fig. 10. This tube can be heated to a low red heat without danger of cracking, or collapsing when evacuated. At this temperature the metallic calcium unites readily with the residual gases, without attacking the quartz-glass tube. If heated to a bright red temperature, the hydrides and nitrides of calcium are dissociated and gases are evolved. On cooling these gases again combine, and, on admitting a small amount of air through the stopcock, it was found that nitrogen, etc., continued to combine with the calcium until the temperature had fallen to about 300°. If the calcium is heated to a very bright red then it, of course, combines chemically with the quartz glass. However, by evacuating the air to a pressure of about 0.1 mm there is no necessity for heating the calcium to a higher temperature than that indicated by the red glow of the quartz-glass tube.

Before closing the container permanently it was found best to evacuate the air to a low pressure and heat the calcium to a bright red, which dissociates the hydrides, etc. The pumping is continued, and air is admitted repeatedly to assist in clearing the water vapor from the walls of the receptacle.

Some of the air admitted combines, of course, with the hot calcium, but that it not detrimental. The quartz-glass tube may become black from the vaporized calcium, as shown in Fig. 10 (this is container No. 7, described in Note 4), but that seems to be beneficial rather than detrimental. In fact, calcium in container No. 6 (see Note 4) was not given this severe preliminary heating before detaching it from the pump, and the best vacuum was produced only after some of the calcium had been vaporized by a subsequent heating to a bright red. The black deposit on the walls of the quartz-glass tube is easily removed by means of soap and water.

⁵⁰ Soddy: *Proc. Roy. Soc.*, 78, p. 429; 1907.

⁵¹ Baly: *Spectroscopy*, p. 433 (new edition).

As mentioned in Note 4, what vapors, if any, were given off by the stopcock grease and the Khotinsky cement were removed by heating the calcium by means of an alcohol blast lamp, which was the most convenient method of heating on a mountain. A small electric heater surrounding the quartz tube might be provided in a permanent laboratory equipment. Now that the device has been shown to be useful, it is possible to eliminate the stopcock, thus removing one source of possible leaking. However, the stopcock is the most useful part of the apparatus in case of breakage, and it is not detrimental to retain it. The stopcock grease used was a haphazard combination of beeswax and mutton tallow (which was too hard for frequent turning of the stopcock), to which had been added a combination of rubber dissolved in vaseline. The latter when used alone was too soft to withstand the pressure upon the stopcock. The whole was heated in vacuo to remove the air, and happened to be an excellent mixture. The Chatterton compound gave off vapors, and hence was used only as an outside cover because of its pliability when subjected to slow changes by expansion and contraction. As mentioned in Note 4, there seemed to be no leaking of air, and the vapors released from within were easily removed. If the receptacles had leaked, all the constituents of the air could have been removed, except argon, of which there would have been an accumulation, which eventually would have been sufficient to reduce the radiation sensitivity of the thermoelements. Judging from the faint bluish discharge in container No. 6, when operated on an induction coil, there was present a small amount of argon, introduced by a temporary leak, as already mentioned.

As to the actual degree of evacuation attained, no exact measurements were made. It was found that after warming the calcium the discharge from a 10,000-volt transformer could not be passed through the tube. At Mount Hamilton the tests were made with a small induction coil operated by two "dry batteries." In this test the discharge would pass through the 5-cm air space between the electrodes P, Fig. 10, in preference to passing through the evacuated space within the tube. With reference to the efficiency of the device it may be added that this evacuator employing calcium to maintain a vacuum was found superior to the carbon electrode evacuator described by Pfund.⁵² In the latter it was found that if the discharge was too vigorous gases would be expelled, which could be removed only by pumping or by heating the calcium evacuator which was tested at the same time. On the other hand, if the calcium be overheated, thus dissociating the hydrides, etc., the gases are again combined on cooling.

⁵² Pfund: *Phys. Z. S.*, 12, p. 870; 1912.

COMBUSTION CALORIMETRY AND THE HEATS OF COMBUSTION OF CANE SUGAR, BENZOIC ACID, AND NAPHTHALENE

By Hobert C. Dickinson

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PART 1

I. INTRODUCTION

The heat of combustion at constant volume of a substance containing only the elements carbon, hydrogen, and oxygen may be defined as the number of heat units liberated by the combination, in an inclosure of constant volume, of unit mass of the substance with oxygen to form carbon dioxide and water, the substance and the oxygen being initially at the same temperature, the products of combustion being cooled to the initial temperature, and the water formed by combustion being condensed to the liquid state. To be exact, the temperature at which the reaction takes place should also be specified, but the change of the heat of combustion with change of initial temperature is so small that this is not necessary for a temperature range between 15° and 30°, temperatures at which experimental results are usually obtained. In practice, also, the initial and final temperatures are not usually the same, but differ by from 2° to 4°. The effect of this difference is also small and is usually neglected, except that it is partly taken account of when the heat capacity of the combustible charge is included in that of the calorimeter. The term "heat of combustion" is also commonly used to denote the heat liberated by the oxidation of substances containing other oxidizable elements, such as sulphur, nitrogen, etc. When the

term is so used, the definition must be extended so as to define the condition of the final oxidation products, as, for example, if sulphur is present, whether the resulting product is sulphur dioxide or sulphuric acid.

Accurate determinations of the heat of combustion of a solid may be made by means of a calorimetric bomb of one of the several recognized types. These various bombs, while differing in mechanical details, consist essentially of a thick-walled metal vessel which can be opened for cleaning and the insertion of the substance, and closed tightly against 30 to 100 atmospheres pressure by means of a cover clamped or screwed in place. There is provision for filling the bomb with oxygen under pressure and for igniting electrically the charge of combustible.

The heat liberated by the combustion within such a bomb is measured by determining the rise of temperature of a known mass of water in which the bomb is immersed.

Apparatus of the above kind is now in use in many commercial laboratories and by users of fuel for the determination of the heats of combustion of fuels as a basis for purchase.

As is often the case where the same operations are repeated many times by the same observer, the relative accuracy (precision) of determinations made under such circumstances is often high, while the agreement between results found at different laboratories (i. e., true accuracy) is sometimes less satisfactory.

In order to make it possible for different laboratories to express results of calorimetric determinations on a uniform and comparable basis, it was deemed desirable to determine accurately the heats of combustion of some chosen substances which can be reproduced with the requisite degree of purity and which can be used for calibrating the various forms of bomb calorimeters in use in commercial laboratories as well as by scientific investigators. This made necessary a careful study of the methods which are in use or which may be adapted for use in fuel calorimetry.

II. METHODS OF BOMB CALORIMETRY

Measurements of heat energy may be carried out by means of observations on the change of state or on the change of temperature of substances. Since only the latter method seems to be

applicable to the problems in hand, that method only will be considered here.

Since there are no perfect heat insulators any calorimetric observation must necessarily involve a correction term to allow for heat transfers which take place within the calorimetric system, or some method must be used for eliminating such heat transfers. To reduce such corrections to a simple and determinate form it is well to consider a calorimetric system as consisting of two essential parts, first, a limited region containing a mass of known heat capacity the temperature of which is either uniform throughout or has some other known distribution as regards space and time; second, a surface surrounding and inclosing this region, and having a temperature either uniform and constant or at least known as regards space and time. The inclosed region will be spoken of as the "calorimeter" and the inclosing surface or vessel as the "jacket."

Four methods are applicable to the measurement of heats of combustion by means of a calorimetric bomb: First, the rise of temperature of the calorimeter, containing a stirred liquid, may be observed while the jacket temperature is kept constant; second, the temperature of the jacket may be kept the same as that of the calorimeter and only the initial and final temperatures measured (this method has been perfected by T. W. Richards at Harvard); third, the temperature of the calorimeter may be kept constant, as, for instance, by supplying cold water at the same time that the heat is being supplied (this method was used by Hesehus, of St. Petersburg, 1888); fourth, the temperature rise of the bomb itself may be measured, depending upon metallic conduction to equalize the temperature throughout its mass. This method has recently been applied by Féry to a specially constructed bomb for fuel combustion.¹ It might be applied with the jacket at a constant temperature or with the jacket at the same temperature as the bomb (calorimeter).

Of these four methods the first two are the only ones which have yet been largely used, and the first is the one which has been and probably will continue to be most used. This method was

¹ Nernst has made use of a similar method during the past few years for the determination of specific heats, and similar apparatus has been in use at the Bureau of Standards for about the same length of time.

adopted for the present investigation, and the discussion of the sources of error on a later page will show that it affords about the same accuracy as the second method.

III. FACTORS AFFECTING ACCURACY

1. **Temperature Measurement.**—By far the most commonly used instrument for measuring temperatures in calorimetric experiments is the mercury-in-glass thermometer. The unavoidable errors of elastic aftereffect, of irregular capillary pressure and sticking of the mercury meniscus are not decreased by making the scale open and the bulb large as in calorimetric thermometers and with thermometers having a scale covering 10° or 15° and graduated to 0.02° the accuracy of a single measurement of a 2° temperature interval is hardly better than 2 or 3 parts in 1000. If a carefully calibrated Beckmann or other metastatic thermometer is used, the accuracy may possibly reach 1 part in 1000, the precision being somewhat higher in both cases. Some better method of temperature measurement is therefore necessary for precision calorimetry. This may be found in the adoption of either thermoelectric² or electrical resistance methods. The former has been brought to a high degree of perfection by White, of the Carnegie Geophysical Laboratory, while the latter has been developed to a very satisfactory condition at the Bureau of Standards and by Jaeger at the Physikalisch Technische Reichsanstalt. By either method an accuracy of 1 or 2 parts in 10,000 in the measurement of the above-mentioned temperature interval is attainable.

2. **Stirring of the Calorimetric Liquid.**—Vigorous stirring of the calorimetric liquid is necessary to keep the calorimeter at a uniform temperature throughout while heat is being rapidly supplied to it. There are two distinct functions of a stirrer, mechanically more or less incompatible: First, the whole mass of liquid in a calorimeter must be circulated, so that there are no stagnant portions; and second, there must be thorough mixing of the different portions of the liquid in order that a measurement of its mean temperature may be given by a thermometer of convenient size. Two forms of stirring apparatus are in general use, the ring stirrer,

² Constancy of Thermoelements, White, *Phys. Rev.*, **22**, p. 449; 1906.

or some modification of it, having a reciprocating motion, and the screw-propeller stirrer. The former mixes thoroughly the smaller portions of the liquid but produces little positive circulation, so that certain portions of the liquid may be left nearly stagnant. It also has the disadvantage that the shaft alternately enters and leaves the surface of the liquid, thus promoting evaporation. The screw-propeller type of stirrer, on the other hand, properly applied, produces a rapid circulation of the whole mass of liquid, but may not so thoroughly mix the different portions—i. e., may permit definite stream lines. Such a stirrer can be mounted on a very small shaft and in such a way as not to promote evaporation.

A careful comparative study of the two methods of stirring, made at the Bureau of Standards by E. F. Mueller,³ showed that the screw propeller produced temperature equilibrium throughout the mass of liquid in about half the time required when the other form of stirrer was used, and that the inequalities which persisted after a given time are very much less with the screw propeller. The energy dissipated by the screw propeller may be also much less than for the reciprocating stirrer. The screw in these experiments was mounted in a calorimeter shaped to adapt it to this type of stirrer. The design was similar to that described on page 210.

3. Heat Transfer Between Calorimeter and Jacket.—Heat transfer between a calorimeter and its jacket may take place in four ways—by conduction, convection, radiation, and evaporation (or condensation). Under ordinary calorimetric conditions some-

³ Mr. Mueller's experiments were made with the ring stirrer, as provided with the Peters calorimeter, and with the screw propeller in the calorimeter mentioned above. The temperatures at various positions in the calorimeter, during and after a period of heating electrically, were determined by means of a differential copper-constantan thermobattery consisting of five elements. One set of junctions was kept fixed while the other was placed in different positions. With the ring stirrer, differences of temperature of $0^{\circ}.5$ were observed one minute after the heating current had been switched off. These differences were reduced to $0^{\circ}.001$ only after from 7 to 10 minutes. Experiments with the screw stirrer, running at normal speed, gave differences of temperature during the first minute of from $0^{\circ}.06$ to $0^{\circ}.08$, or only about one-tenth as great as with the ring stirrer. These differences were reduced to $0^{\circ}.001$ within about 5 or 6 minutes after shutting off the heating current. It was also found that with the screw stirrer there was only a very small portion of the calorimeter which showed this lag in coming to temperature equilibrium, while with the ring stirrer a considerable part of the water was involved in the lag. The calorimeter, B. S. 7602, described on page 212, has a screw of larger diameter, which is run at slower speed than the one examined and the temperature of the water, as indicated by the resistance thermometer, appears to reach equilibrium to $0^{\circ}.0002$ within one minute after heating has ceased, when there is no large mass of metal, such as a bomb, which may cause a lag apart from that due to the stirring.

thing like one-fifth of the heat is transferred by radiation, about four-fifths by convection and air conduction, and only a very little by evaporation.

In the calculation of corrections for the transfer of heat it is generally assumed that Newton's law of cooling holds over the small range of temperature in question. That this assumption is only approximately true has been shown repeatedly by experiment and can be seen from theoretical considerations. In so far as radiation is involved the heat transfer is proportional to the difference of some higher power (about the fourth power) of the absolute temperatures of the two surfaces.

The heat transfer by convection and air conduction can hardly be considered from a theoretical basis, because it depends largely upon the shape and size of the surfaces involved. For small temperature differences, however, Newton's law is a very close approximation.⁴ The transfer of heat by conduction and convection is nearly proportional to the temperature difference after steady state is reached.

With the heat transfer by evaporation and condensation, however, conditions are very different. If a free liquid surface forms part of the calorimeter and no corresponding free liquid surface is present at the temperature of the jacket, there will be no transfer of heat by evaporation so long as the calorimeter temperature is sufficiently below that of the jacket, as there will be no condensation of vapor on the warmer surface, and there will be no vapor lost to the space outside if the jacket is closed; but when the temperature of the calorimeter rises above that of the jacket, vapor is condensed on the cooler surface of the jacket and supplied from the free liquid surface, taking heat from the calorimeter. There is thus only a very small loss of heat from the calorimeter, due to the formation of enough vapor to keep the surrounding space saturated at the rising temperature until the temperature of the calorimeter is near that of the jacket, then there is increasing loss of heat by evaporation as the temperature rises. Since this heat

⁴ Some later observations have shown that this is by no means as nearly true when there is a considerable air space between the calorimeter and the jacket as it is in the present calorimeter, where the air space is reduced to a uniform width of about 1 cm.

transfer does not follow a simple law, it should be prevented so far as possible.

Observations have shown that the assumption of Newton's law or that $\frac{d\theta}{dt} = -k(\theta - \theta_0)$ where θ is the temperature of the calorimeter, θ_0 the temperature of the jacket, t the time, and k a constant, is justified for ranges of a few degrees in temperature provided k is determined from observations taken at the two temperatures between which the formula is to be applied. In most calorimetric measurements, however, the principal quantity observed is a temperature change produced mainly by energy liberated or absorbed within the calorimeter, while the above equation, representing the assumption usually made, takes account of only such temperature changes as are produced by convection, air conduction, radiation, etc. The complete differential equation for the temperature in a calorimetric observation would be $\frac{d\theta}{dt} = f(t) - k(\theta - \theta_0)$ where $f(t)$ is the rate of temperature change produced by the energy supply which is the subject of the experiment. The integral of this is the main quantity to be measured and is usually much larger than the term $k(\theta - \theta_0)$, which is a correction term. The assumption $k = \text{constant}$ permits the simple solution:

$$\theta = \theta_0(1 - e^{-kt}) + \int_0^t f(t) dt$$

when $\theta = 0$ and $f(t) = 0$, at time $t = 0$. The temperature at any time is simply the original temperature plus the temperature change due to the heat supplied plus the cooling correction. However, if k is a function of time, the equation can not in general be solved. The solution would take the form

$$\theta = \theta_0(1 - e^{-\int k(t) dt}) + e^{-\int k(t) dt} \int_0^t e^{\int k(t) dt} f(t) dt$$

in which $k(t)$ occurs in the main term, so that even an approximate solution is not easily obtained. The value of k can in general be determined only at times when the term $f(t) = 0$ and the fact that observations taken under these conditions indicate that

the assumption $k = \text{constant}$ is sufficiently accurate, by no means proves that the same assumption is justified when $f(t)$ is large, i. e., when the rate $\frac{d\theta}{dt}$ is large.

It will be seen in the following discussion that k in the above equation is a function of the time, $k(t)$, to an extent which can not be neglected unless certain conditions are fulfilled. Of the four modes of heat transfer, radiation alone can physically correspond to the condition $k(t) = \text{constant}$ (i. e., k independent of time). The effect of evaporation can be eliminated. The effect of conduction and of convection on $k(t)$ will be considered separately.

4. Conduction and its Effect on $k(t)$.—Although the amount of heat transferred between calorimeter and jacket by conduction other than through the air is usually small, under certain conditions the effect on k may be very large. For example, if two objects placed on opposite sides of a plate of insulating material are at different temperatures, the rate of heat transfer between them—therefore the rate of temperature change of either with respect to the other (neglecting outside influences)—will become sensibly proportional to the temperature difference. If, however, the temperature of either is changing rapidly, due to an external cause, the rate will no longer be even approximately proportional to the temperature difference.

The most common cause of errors due to conduction is the presence of a sheet of poorly conducting material interposed between the calorimeter and the jacket, as when the calorimeter is supported on a rubber or cork block, or when an attempt is made to reduce the heat transfer by using some form of insulating material, as was often done up to a few years ago. Since the conductivity of such materials is always small, compared with that of the metallic sheets in contact with them, the temperatures of the surfaces may be taken, for the purposes of this discussion, as approximately the same as the measured temperatures of the calorimeter and the jacket, respectively. The distribution of temperature in such a layer and the rate at which heat is leaving the calorimeter at any time may then be determined from the following considerations:

A sheet of material of thickness c bounded by plane surfaces x_0 and x_1 , is initially at temperature θ_0 . If x_0 and θ_0 are each taken as 0 for convenience, and the temperature of one of the surfaces x_1 is then caused to rise from θ_0 to θ' in such a way that $\theta = \theta' (1 - e^{-\alpha t})$, the temperature distribution in this plate is given by the following:⁶

$$(1) \quad \theta = \frac{x}{c} \cdot F(t) + \frac{2}{\pi} \sum_1^{\infty} \left[\frac{(-1)^m}{m} \sin \frac{m\pi x}{c} \left(F(t) - \frac{m^2 a^2 \pi^2}{c^2} \int_0^t F(\lambda) e^{-\frac{m^2 a^2 \pi^2}{c^2} (t-\lambda)} d\lambda \right) \right]$$

Where a^2 is the *thermometric* conductivity of the material.

$F(t)$ is the temperature of the face $x_1 = c$, taken here as $\theta' (1 - e^{-\alpha t})$.⁷

The point of interest in this discussion is the rate at which heat is leaving the calorimeter at any time, as this determines the value of k for the portion of the surface in question. If θ' and c are each made unity, and the above expression for θ is differentiated with respect to x , the following expression for the temperature gradient at any point in the material is found:

$$(2) \quad \frac{d\theta}{dx} = 1 - e^{-\alpha t} + 2 \sum_1^{\infty} (-1)^m \cos m\pi x \left(e^{-\alpha t} - e^{-\frac{m^2 a^2 \pi^2}{c^2} t} \right) \frac{\alpha}{m^2 \pi^2 a^2 - \alpha}$$

The surface $x = 1$ is the surface in contact with the calorimeter, so that substituting this value of x and the appropriate values for a^2 and α , the above expression gives the temperature gradient in the material in contact with the calorimeter, which is proportional to the factor k for this portion of the surface.

For an example showing the effect of this kind of distribution of material, suppose that the calorimeter rests on a sheet of hard rubber 1 cm. thick. The temperature in the calorimeter used for the present investigation, when containing a bomb in which a

⁶ Byerly; *Fourier's Series and Spherical Harmonics*, p. 110.

⁷ This equation represents quite approximately the temperature rise of a calorimeter containing a combustion bomb in which a charge is burned.

charge of combustible is burned, rises quite approximately according to the relation $\theta - \theta_i = (1 - e^{-\alpha t}) (\theta_1 - \theta_i)$ where $\alpha = 0.03$ and θ , θ_1 , and θ_i represent, respectively, the temperature at any time, the initial, and final temperature. The value of a^2 , the thermometric conductivity, for hard rubber is approximately 0.001 in cgs units. These quantities substituted in the above equation show that after 60 seconds the rate of heat loss is 2.75 times its final value, after five minutes the rate is 1.13 times the final value, and only after 10 minutes does it come to within 1 per cent of its final value. If the area in contact with such a sheet were a considerable part of the whole area of the calorimeter, the error introduced from this cause evidently would be a very serious one.

Such a distribution of material as here discussed will also have an effect on the heat capacity of the calorimeter, similar to that discussed on page 204 et seq.

This discussion shows that all nonconducting supports should be negligibly small or, since the thermometric conductivity $a^2 = \frac{K}{c\rho}$ (the absolute conductivity K divided by the specific heat (c) and density (ρ)), the material used for them should have a small density and specific heat. A form of support is therefore indicated, in which the smallest possible mass of insulating material is used, with the smallest possible area in contact with the calorimeter. The mass of such supports can readily be made negligible compared with that of the calorimeter.

5. Convection and Radiation, and their Effects on $k(t)$.—Since the greater part (about 4/5) of the transfer of heat between a calorimeter and its jacket is generally due to convection and conduction in the intervening layer of air, it is important to consider the nature and rate of establishment of convective equilibrium. Evidently the establishment of complete equilibrium for any given temperature distribution requires time. Hence, if the temperature distribution is rapidly changing, this equilibrium will not be established, or rather will lag behind the temperature distribution over the surfaces and the observed value of $k(t)$ may be in error. This subject can not readily be treated from a theoretical basis and an experimental investigation of it is given on a later page.

With some distributions of material, however, the value of k may be dependent upon the time, because of both convection and radiation. Consider a calorimetric system in which certain masses of material, with considerable area and good conductivity, are interposed between the calorimeter and the jacket, such, for instance, as metallic shields to decrease radiation, or parts of the jacket not maintained at a definite temperature, but allowed to take up a temperature dependent upon the surroundings. It will be assumed that the rate at which heat passes between a calorimeter and its jacket is dependent upon the nature and form of the surfaces and the temperature differences, and not very much upon their distance apart unless this distance becomes small. In a calorimetric system of the usual dimensions the air space, as found by experience, should not be much less than 1 cm in width for this assumption to hold.

Suppose a mass m of material, the specific heat of which is c' and the superficial area is s , situated in the neighborhood of other surfaces, in the present case two, one of which is at constant temperature and the other at a temperature which may be changed. If the system is initially in a steady state and the temperature of one of the surfaces is suddenly changed to another steady value, the mass m will eventually take up some temperature differing from the initial one and depending upon the existing distribution of temperature in the system. Let this equilibrium temperature be θ_e , then the temperature θ of the mass m at any time will be given by a solution of the equation $\frac{d\theta}{dt} = -\phi(\theta - \theta_e)$; that is, $\theta = \theta_e + ce^{-\phi t}$. If $\theta = 0$ when $t = 0$, the equation gives $\theta = \theta_e(1 - e^{-\phi t})$. If ϕ' and ϕ'' are respectively the cooling constants of the mass m with respect to the calorimeter, and the jacket, and θ' and θ'' are the temperatures of the calorimeter and the jacket, the equilibrium temperature θ_e of m will be given by the relation

$$(\theta' - \theta_e)\phi' = (\theta_e - \theta'')\phi''$$

$$(3) \quad \text{whence } \theta_e = \frac{\theta' \phi' + \theta'' \phi''}{\phi' + \phi''} \quad \text{or if } \theta'' = 0, \theta_e = \frac{\theta' \phi'}{\phi' + \phi''}$$

For instance, if the calorimeter, the shield (m), and the jacket were concentric spherical surfaces, ϕ' would be nearly propor-

tional to the solid angle subtended by the calorimeter at m and ϕ'' to the angle subtended by m at the jacket. If ϕ is nearly independent of distance, since the temperature of m at any time is $\theta = \theta_e(1 - e^{-\phi})$ and the temperature of the calorimeter is θ' , the rate of temperature change of the calorimeter due to the presence of m alone is as follows:

$$(4) \quad \left(\frac{d\theta'}{dt}\right)m = -h\phi'(\theta' - \theta)$$

where h is the ratio of the heat capacity of m to that of the calorimeter, and the change in θ' is small compared with the quantity $(\theta' - \theta)$. Substituting the values of θ and θ_e from the foregoing equations

$$\begin{aligned} (5) \quad \left(\frac{d\theta'}{dt}\right)m &= -h\phi' \left[\theta' - \theta_e (1 - e^{-\phi}) \right] \\ &= (-h\phi') \left[\theta' - \frac{\theta' \phi'}{\phi' + \phi''} (1 - e^{-\phi}) \right] \\ &= -h \left[\frac{\theta' \phi' \phi''}{\phi' + \phi''} (1 - e^{-\phi}) \right] \end{aligned}$$

The above equations show some interesting facts. If m is a sheet halfway between extended parallel surfaces of the calorimeter and the jacket and not too near either, $\phi' = \phi''$, the loss of heat from the calorimeter over this portion of the surface will, by equation 3, be half of what it would be if the sheet were not there, since the temperature difference between the calorimeter and m is only half that between the calorimeter and the jacket. This will be approximately true when the outside area of the calorimeter is not much less than that of the jacket. The errors which may be introduced, however, by an attempt to utilize this fact for reducing the rate of heat loss are evident from the following example:

A sheet of metal having a heat capacity of 0.8 calorie per cubic centimeter per degree, a thickness of 0.03 centimeter and polished surfaces from which heat will be lost by radiation, conduction, and convection at the rate of 0.0001 calorie per

second per square centimeter per degree difference in temperature, will have a cooling constant $\phi = 0.012$ degree per second. Substituting this value of ϕ in the above equation for rate of temperature change, the rate four minutes after the calorimeter temperature is changed from 0° to 1° will be 10 per cent, and after eight minutes 1 per cent greater than the final value. The same sort of an effect is present whenever the temperature of either the calorimeter or the jacket is changed.

The above figures would apply approximately to a calorimeter placed within a thin metallic vessel, when the walls of the room correspond to the constant temperature jacket. The conditions may be even worse when the containing vessel is of insulating material, such as a fiber pail, the kind of vessel often used for this purpose. With any such arrangement the cooling constant is a function of the time to a serious extent.

Ordinarily for precise observations the calorimeter is surrounded by a double-walled metallic vessel containing a large mass of water, preferably kept stirred. The inner surface of this metallic vessel is properly considered as the constant temperature jacket. This outer vessel can, however, evidently be considered as m in the above treatment, the walls of the room being taken as the constant temperature jacket. The heat capacity of such a double-walled vessel is from 200 to 400 times as great as for the metallic sheet discussed above, and in this case ϕ (the reciprocal of the time lag) becomes so small (about 0.00003) that the term $(1 - e^{-\phi t})$ is practically 0; i. e., the change of temperature in 10 minutes is about 2 per cent of the total change which would take place. This is generally unimportant and can be corrected for if necessary. Such a jacket as this, however, is often provided with a cover of thin hard rubber or other material which is not kept at the temperature of the jacket itself. The effect of such a cover on the value of k can be seen from the above considerations.

The foregoing discussion shows that although Newton's law may represent with sufficient accuracy the behavior of a calorimeter when no heat is being produced or absorbed within it, the additional assumption that the same expression may be used for the heat interchange between the calorimeter and its sur-

roundings, when heat is being produced or absorbed within, is not in general justified. In order that this assumption shall be justified it is necessary that any mass of material between the calorimeter and the jacket which may possess an indefinite intermediate temperature shall be small or that the difference in temperature between it and either the calorimeter or the jacket shall be small.

6. Lag of Thermometer.—In the foregoing discussion it has been assumed that the thermometer immersed in the calorimeter measured at every instant the true temperature of the outer wall of the calorimeter. This is never strictly true on account of the so-called time lag of the thermometer and of the calorimeter wall. If the calorimeter liquid is vigorously stirred and the material of the walls is thin and of high conductivity, probably the lag of the outer surface behind the temperature of the liquid itself is negligible. The lag of mercurial thermometers, which are suitable for calorimetric observations, is, however, from 5 to 8 seconds. The time lag of a thermometer may be defined as the number of seconds intervening between the time that the uniformly rising temperature of a given medium reaches a certain value, and the time that the thermometer immersed in that medium indicates this same temperature. It is not a constant for a given thermometer but depends upon the nature and rate of stirring of the medium in which the thermometer is immersed. As the rate of stirring increases the lag of a given thermometer approaches a constant value. In the case of the resistance thermometers, to be described later, the lag has been reduced probably to less than 0.5 second, but since the corresponding lag of the galvanometer used in measuring the resistance is approximately two seconds, this practically determines the time lag of the temperature-measuring system.

White⁷ has shown that the lag of the thermometer introduces no error in the results of a calorimetric observation, provided the same thermometer is used throughout the observation. The subject of thermometric lag has been considered in detail by Harper.⁸

⁷ *Phys. Rev.*, **21**, p. 562; 1910.

⁸ *This Bulletin*, **8**, p. 699; 1912 (Reprint No. 185).

7. Boundary of the Calorimeter.—The heat capacity of a calorimeter at a given temperature may be defined as numerically equal to the number of heat units required to raise the temperature of the calorimeter 1° at this temperature.

The discussion on pages 198 to 203 indicates the effect of matter distributed between the calorimeter and the jacket, on the time required for the establishment of temperature equilibrium. It is evident, however, that such matter, independently of the time it takes to reach equilibrium, affects the heat capacity of the calorimeter as defined above. Referring to page 200, it will be seen that when the temperature of the calorimeter rises from 0 (that of the jacket) to θ' , the temperature of the conducting mass between the calorimeter and the jacket eventually rises

from 0 to $\frac{\theta'\phi'}{\phi'+\phi''}$, and if its mass is m and its specific heat is c ,

an amount of heat $mc \frac{\theta'\phi'}{\phi'+\phi''}$ has been taken from the calorimeter in establishing such temperature equilibrium. The heat capacity of the calorimeter is therefore increased by an amount

$\frac{mc\phi'}{\phi'+\phi''}$ on account of the presence of the mass m , since $\frac{\phi'}{\phi'+\phi''}$ is the rise of temperature of m per degree rise of temperature of the calorimeter. If the mass m is in the form of a sheet or rod of uniform section extending between the calorimeter and the jacket (considering conduction only)—i. e., neglecting radiation— $\phi' = \phi''$ and the amount to be added to the heat capacity is $\frac{1}{2} mc$.

It is necessary in practice to have certain masses, such as a thermometer stem, stirring shaft, and electrical connections, which extend from the calorimeter. If such parts pass through the jacket and are kept at the temperature of the jacket where they enter it on the side toward the calorimeter, their effect on the heat capacity is that just discussed, i. e., neglecting the effect of radiation, etc., which would, in general, be small, there must be added to the heat capacity a correction, $\Sigma \frac{1}{2} mc$.

If, however, such extensions from the calorimeter are long and the outer portions reach equilibrium with the surrounding air—i. e., if they pass out through free openings in the jacket—

the amount which needs to be added to the heat capacity of the calorimeter to correct for them can be computed in the following manner:*

If the calorimeter is at a given temperature and the portion extending from it into a medium at a different temperature is uniform in section and the temperature can be taken as uniform over any cross section, after equilibrium is reached, the temperature at any distance, x , from the calorimeter is given by a solution of the equation

$$\frac{d^2\theta}{dx^2} = a^2\theta \quad \text{where } a^2 = \frac{HP}{KA}$$

in which H is the surface emissivity (about 0.0001 cal. for polished nickel or copper).

P is the perimeter of the section,

K is the absolute conductivity,

A is the area of the section.

If the outside temperature is 0 and that of the calorimeter is θ' , the required solution is

$$\theta = \theta' e^{-ax}$$

If the temperature of the calorimeter was initially 0 and was raised to θ' , the temperature of the extending rod is also raised, and the heat necessary to raise the temperature of any section dx from 0 to θ is

$$\theta \rho c A dx$$

where ρ and c are the density and specific heat of the material. The total amount of heat Q taken from the calorimeter is, substituting for θ the value given above,

$$\begin{aligned} Q &= \int_0^\infty \theta' \rho c A e^{-ax} dx \\ &= \frac{1}{a} \theta' \rho c A = \theta' \rho c A \sqrt{\frac{KA}{HP}} \end{aligned}$$

* In this discussion it is assumed that the heat capacity of the calorimeter before correcting for any extended or extraneous matter is the heat capacity of the material comprised within the constant temperature surface which has been defined as the calorimeter.

but the heat required to raise the temperature of unit length of the material from 0 to θ' is $\theta' \rho c A$, so that a length $\sqrt{\frac{KA}{HP}}$ of this material must be considered as a part of the calorimeter, i. e., the heat capacity must be increased by $A \rho c \sqrt{\frac{KA}{HP}}$ on account of the presence of this extended portion.

For example, a copper wire of circular section 2 mm in diameter dipping into a calorimeter would add to the heat capacity an amount equal to nearly 7 cm of the wire, i. e., about 0.2 gram of water, since H for bright copper is 0.0001, K is 0.9, and $\frac{A}{P} = \frac{r}{2}$.

8. Richards's Method of Avoiding Cooling Corrections.—This method, as mentioned before, consists in causing the temperature of the jacket to be continually equal to that of the calorimeter. A consideration of the foregoing discussion as to the effect of various distributions of material on the cooling rate and heat capacity of the calorimeter, will show that most of the errors and uncertainties would remain nearly the same in this as in the foregoing method of procedure, but the errors due to these causes can be made negligibly small in either case. The relative accuracy of the method of constant jacket temperature and the method of varying jacket temperature reduces nearly to a question of the accuracy of observing a rapidly rising temperature relatively to that of keeping the temperature of a second mass of liquid always the same as the rapidly rising calorimeter temperature. The time lag of the thermometric device has been shown to introduce no appreciable error. The Richards method has the apparent advantage that the initial and final temperatures are constant while in the other method they are slowly changing. This is not advantageous with mercurial thermometers but is so with resistance thermometers or thermocouples. Even if there is some advantage in constant initial and final temperatures it would seem that this advantage may be offset by the unavoidable errors in causing the temperature of one bath to remain constantly equal to that of another, which is changing rapidly in a manner which can not always be readily predicted. In order to maintain the required condition of temperature equality it is necessary either to

know the form of the arbitrary function representing the rise of temperature of the calorimeter or to follow it with some thermometric device, constantly adjusting the jacket temperature to it; but these operations are equivalent respectively to the thermometric problem of plotting the mean form of the arbitrary temperature rise or plotting its form for a given observation. Any error in maintaining the required temperature in the jacket therefore seems to be added to the errors inherent in the constant jacket temperature method, unless the temperature difference between the calorimeter and the jacket is determined at frequent intervals and a cooling correction applied. When a chemical reaction takes place similarly at the same time in the calorimeter and jacket, the varying jacket temperature has advantages in convenience and perhaps in accuracy. When correction is made for temperature difference, as described above, this method is also advantageous where very large temperature intervals are used or where long-time intervals are required or where electrical calibration methods are used in such a way as to permit of raising the temperature of the calorimeter and the jacket at the same, nearly linear, rate.

9. Lag of Convection Currents.—The effect of the time lag of convection currents in the air has been referred to previously. (See p. 199.) This lag can not be computed from present knowledge of the properties of the air layer, and its magnitude has theretofore been largely a matter of conjecture. The uncertainties in calorimetric measurements from this cause may be negligible, but seem not to have been investigated.

If it is assumed that the heat transmitted between two surfaces near together is proportional to the mean temperature gradient in the layer of air between them, then, if the temperatures of two different portions of the air layer, one near each surface, can be determined, the rate of heat transfer between the two surfaces at any time may be computed from this observed temperature difference. Such measurements of the temperature of the air can be made by measuring the resistance of very fine wires exposed to the air. Moreover, if platinum wires, the surface of which is nearly like that of the calorimeter and jacket, are used for this purpose, the effect of radiation on their temperature should not affect the validity of the assumption that the difference of temperature

between the wires is proportional to the heat transfer between the surfaces, since this assumption would be true for the effect of radiation alone.

A differential thermometer was built to fulfill the above necessary conditions. The thermometer consisted of two platinum wires 0.05 mm in diameter and about 20 cm long stretched between small ivory supports in such a way that when placed between the calorimeter and jacket the two wires were about 1 mm distant respectively from the surface of the calorimeter and the surface of the jacket. The two wires were connected in adjacent arms of a Wheatstone bridge, so that the difference of their resistances was directly measured.

A series of observations was made with this differential thermometer and the results are shown on Fig. 10, explained on page 222. This series of observations showed that during the middle period the differential thermometer indicated a given temperature difference two and one-half seconds later than did the calorimeter thermometer. The effect of an error of two and one-half seconds in the time of all observations during the middle period would be to introduce an error of about 7 parts in 100 000 in the results. But the lag of convection currents seems to be somewhat, if not entirely, analogous to that of calorimetric thermometers, which itself produces no error in the results. For this reason it is assumed that the lag of convection currents in the present calorimeter produces no error greater than 7 parts in 100 000.

The above experimental method required that the thermometric lag of the differential and the calorimeter thermometer be the same, as was the case in this instance since the same galvanometer was used with both, and the lag of either thermometer of itself was negligible.¹⁰

IV. PRINCIPLES OF CALORIMETRIC DESIGN

1. **General Requirements for a Stirred Liquid Calorimeter.**—Such a system should consist of a calorimeter the outer surface of which has always at all points the same temperature as has the

¹⁰ The lag of the differential thermometer computed from the heat capacity of the wire and the energy required to hold it at a given temperature, above that of the air, is of the order of 0.01 second. The lag of the calorimetric resistance thermometer has been discussed.

liquid within, and a closed jacket which has always and at all points a temperature either constant or equal to that of the surface of the calorimeter, or a temperature uniform over the surface and which is known at all times. The calorimeter should be separated from the jacket by a distance of about 1 cm and held in place in such a way that the materials between them shall have a negligible or at least calculable time lag in coming to temperature equilibrium. These materials should also have a heat capacity negligible, or as small as possible, since their heat capacity enters as a rather uncertain addition to that of the calorimeter. The liquid within the calorimeter should be the standard substance—water—and should be so well stirred that its temperature is always sensibly uniform throughout. The amount of energy used in stirring should be constant and as small as possible. The entire surface of the calorimeter should be in contact with the liquid and no considerable part of the liquid surface should be exposed to permit evaporation, or if any part is so exposed, its temperature should never exceed that of the jacket, unless conditions are carefully considered to make sure that the effect of evaporation is negligible.

2. Size of the Calorimeter.—The choice of size for a calorimeter is determined by the relative accuracy attainable in the measurement of certain quantities. The heat capacities of similar calorimeters are proportional to L^3 where L is a linear dimension, the cooling surface to L^2 , and the rise of temperature to L^{-1} . Taking the supply of energy to be constant, as must be done in the present case, for a given combustion bomb, the percentage heat interchange is proportional to L^{-1} . The ratio of the heat loss to the total heat supplied is inversely proportional, therefore, to the dimensions. In addition the assumption of Newton's law of cooling is probably more nearly correct for small temperature differences. From this it appears that the controlling factor in determining the dimensions of a calorimeter, once the supply of energy is known, is the accuracy of the temperature measuring device. The dimensions should be such that the temperature rise is as small as can be measured with the required accuracy, with the thermometric apparatus to be used.

V. THE CALORIMETRIC SYSTEM USED

The principles stated in the previous pages have been applied in the construction of two calorimetric outfits and in the adoption of methods which are to be described. Figs. 1 and 2 show sectional views of the elevation and plan of the second of these calorimeters, B. S. 7602, with its jacket and immediate accessories. The earlier form was similar to this, except for details which have greatly increased the convenience of operation and have somewhat increased the precision of observations.

1. *The Calorimeter Proper.*—The calorimeter C is made of thin copper, in the form shown in Fig. 3, to facilitate stirring. The extended portion which contains the stirrer S, Fig. 2, is separated from the main body of the vessel except near the top and bottom, forming a tube, the bottom of which is inclined and curved so as to direct the downward stream from the stirrer smoothly into the main body of the calorimeter. The stirrer S consists of a thin shaft of gold-plated steel on which is mounted a screw propeller made entirely of copper, except for a trifle of solder, and gold plated. The part of the calorimeter over the stirrer is closed by means of a copper cover having an opening only large enough for the stirring shaft. The stirrer thus always remains in the calorimeter.

Since it is important to avoid, so far as possible, evaporation of the calorimeter liquid, the main portion of the calorimeter, which must be accessible, is provided with a cover (Fig. 3 L) which fits the calorimeter vessel closely and has three openings, one for the thermometer and two for leads to the bomb or to the resistance coil M used in calibration. From the previous discussion it is evident that this cover should be in contact with the water. The cover is therefore made in the form of an inverted open dish with collars soldered around the necessary openings. The material is very thin copper.

All the copper surfaces are nicked and polished to reduce radiation. There are no parts such as hooks or handles extending from the calorimeter and no part except the small cover at S and the necessary margin of a few millimeters at the top which is not in contact with the stirred liquid. The temperature of the outer

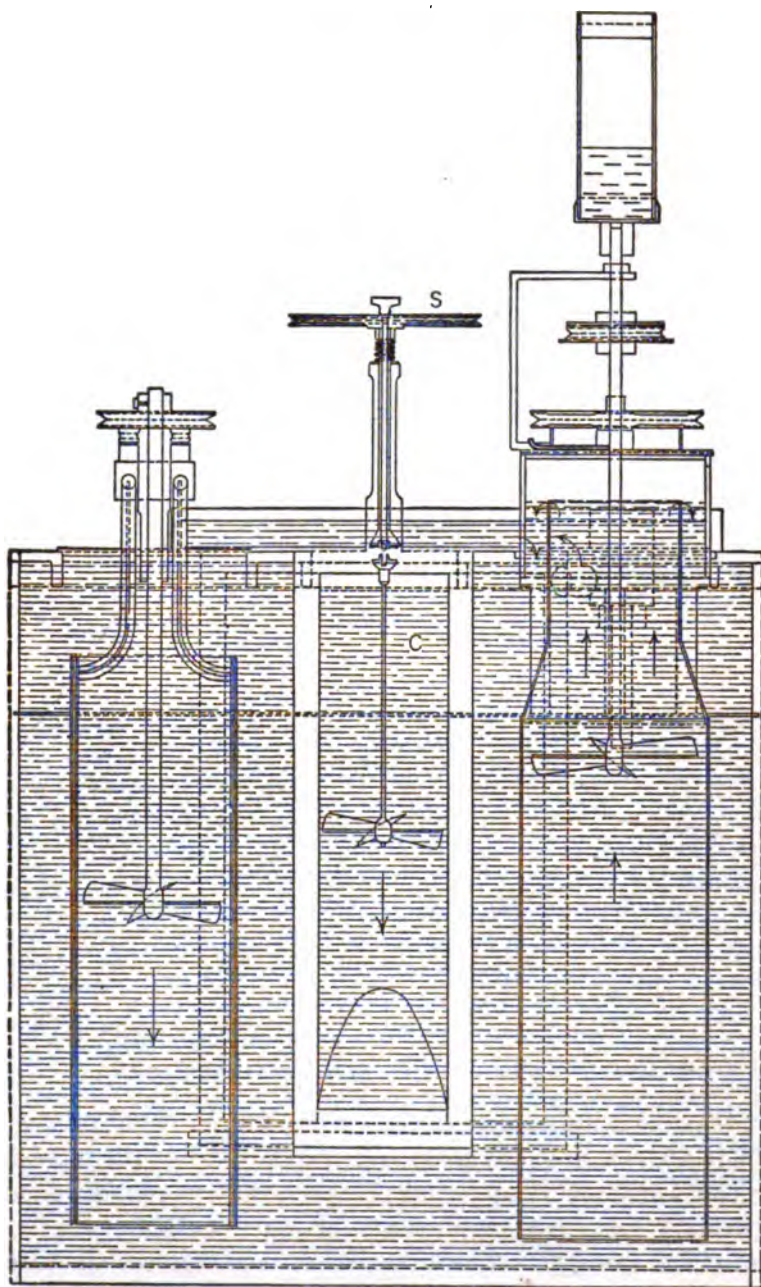


FIG. 1.—Section of calorimeter and jacket

surface can not, therefore, differ greatly from that of the liquid within.

During the process of building the calorimeter and the coil M (Fig. 3) which is used with it, the materials, almost entirely copper, which entered into the construction, were carefully weighed in

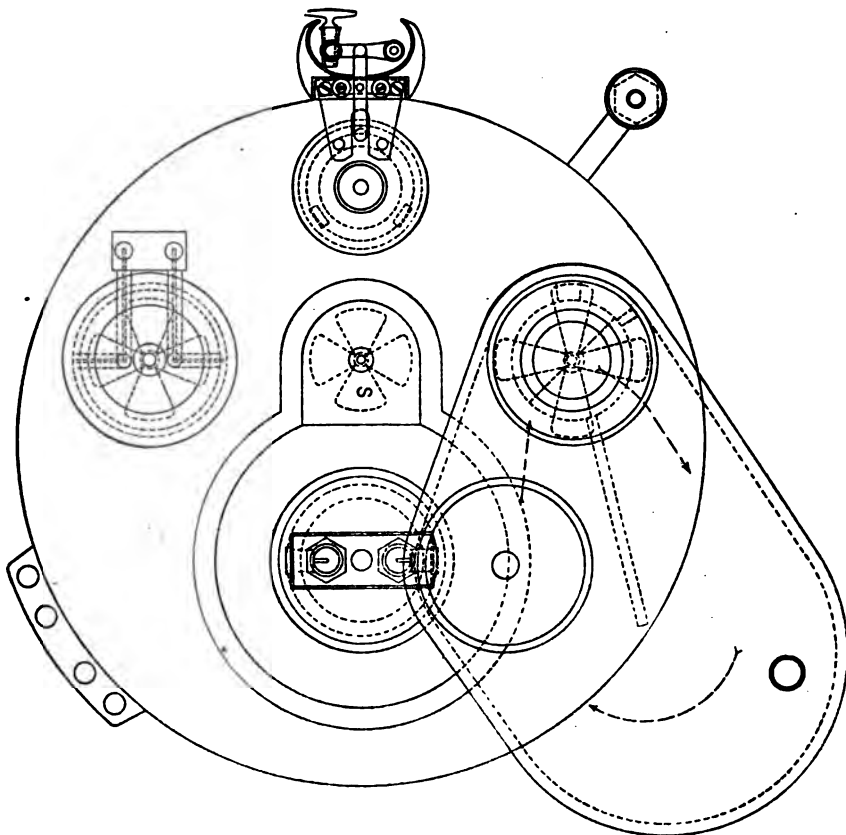


FIG. 2.—Plan of calorimeter and jacket showing bomb in place

order that the heat capacity of these parts which are not removable might be known from the mass and specific heat of the materials.

2. The Constant Temperature Jacket.—The required constant temperature surface is supplied by the inner surface of the water jacket (Figs. 1 and 3). The distance between this and the surface of the calorimeter is approximately 1 cm at all points.



FIG. 3.—Parts of calorimeter B. S. 7602 and accessories

T, thermostat. H, heating coil for jacket. M, heating coil for calibration of calorimeter. Q, current and potential leads in flat plate. D, displacement buoy. C, calorimeter. L, handle for same. B, bomb B. S. 6316



FIG. 4.—Assembled calorimeter B. S. 7602, showing stirring motor and calorimetric resistance thermometer

The jacket must be so arranged that its temperature can be controlled, or at least measured. For convenience as well as accuracy it is desirable that this temperature be kept constant, unless it is desired to make observations by the so-called adiabatic method, in which case the temperature of the jacket must be under control. To provide for either condition the water jacket, as shown in Fig. 1, is provided with a cover through which the water is circulated, a heating coil, H, Fig. 3, having a capacity of at least 2 kilowatts and a thermostat, T, which may be used to maintain any desired temperature from room temperature up to 90° C. (See also Fig. 4.)

3. Supports and the Space between Calorimeter and Jacket.—It was shown that material between calorimeter and jacket may seriously affect the accuracy of the calorimetric measurements. The present construction is intended to reduce the amount of this material and its effect to a minimum. The surrounding air layer is reduced to a thickness of 1 cm and a mass of about 1.5 g, its heat capacity is therefore about 0.3 g.

The largest mass of material in this space is that required for supporting the calorimeter. The supporting pieces (three in number) are each made up of a brass cone soldered to the bottom of the jacket, and a small ivory tip about 2 mm in diameter cemented into the end of the cone and resting against small plates (one with a hole, one with a slot, and the third plane) on the bottom of the calorimeter. The thermal conductivity of the ivory tips is small, and their total mass is not over 0.1 g, so that their effect on the cooling rate is too small to be significant. The brass cones, while they have a considerable mass, have a heat conductivity so great compared with the amount of heat which they can receive by radiation, convection, etc. (about 0.0001 calorie per square centimeter per second per degree temperature difference), that their temperature is at all times measurably that of the jacket,¹¹ hence their effect is entirely negligible, both as regards cooling rate and heat capacity.

¹¹ If a brass rod 2 mm in diameter were soldered to the jacket and extended for 1 cm inside, the temperature at the extremity would differ from that of the jacket by only 5 per cent of the difference between that of the jacket and that of the air within. For the cones the extremities are even nearer the jacket temperature.

The steel stirrer shaft which enters the calorimeter ends just above it in a thin hard-rubber sleeve, which fits tightly over it and tightly within a larger steel piece. The latter couples to the steel shaft which has its bearing in the jacket cover and serves as the only support for the stirrer. (See Fig. 1, elevation.) The stirrer touches nothing within the calorimeter but water. It is evident that since the heat conductivity of steel is many times greater than that of the hard-rubber sleeve, the temperatures of the two metal parts will remain very nearly the same as the temperatures of the calorimeter and the jacket, respectively. The heat capacity of the rubber sleeve, some of which should be added to that of the calorimeter, is insignificant.

Aside from the stirring shaft and the calorimeter supports, the thermometer stem with its four copper leads, and the leads to the heating coil or to the firing terminals of the bomb, are to be considered.

The stem of the thermometer is of thin glass and its effect may be neglected, provided that the proper amount of it is added to the heat capacity of the calorimeter. The leads, however, are inclosed within this glass tube and extend from the calorimeter through the cover to the outer air. They therefore conduct heat between the calorimeter and the room. In this respect, therefore, the jacket is not strictly an isothermal surface and the cooling rate of the calorimeter is to a slight extent dependent upon conditions outside of this surface. The magnitude of this effect will be discussed later.

The coil leads and firing leads, where they pass over the top of the jacket, are in the form of wide, thin copper strips insulated with mica. They rest in good contact with the top of the jacket and are protected from the effect of the room temperature by a felt cover.

4. Accessories.—(a) *Thermometric.*—The platinum resistance thermometer shown in Fig. 6 represents one of four similar thermometers which were built especially for calorimetric work of this kind and are described in this Bulletin, volume 9, page 43, 1913. They resemble in general construction the two thermometers described in this Bulletin, volume 3, page 641, 1907, but have been

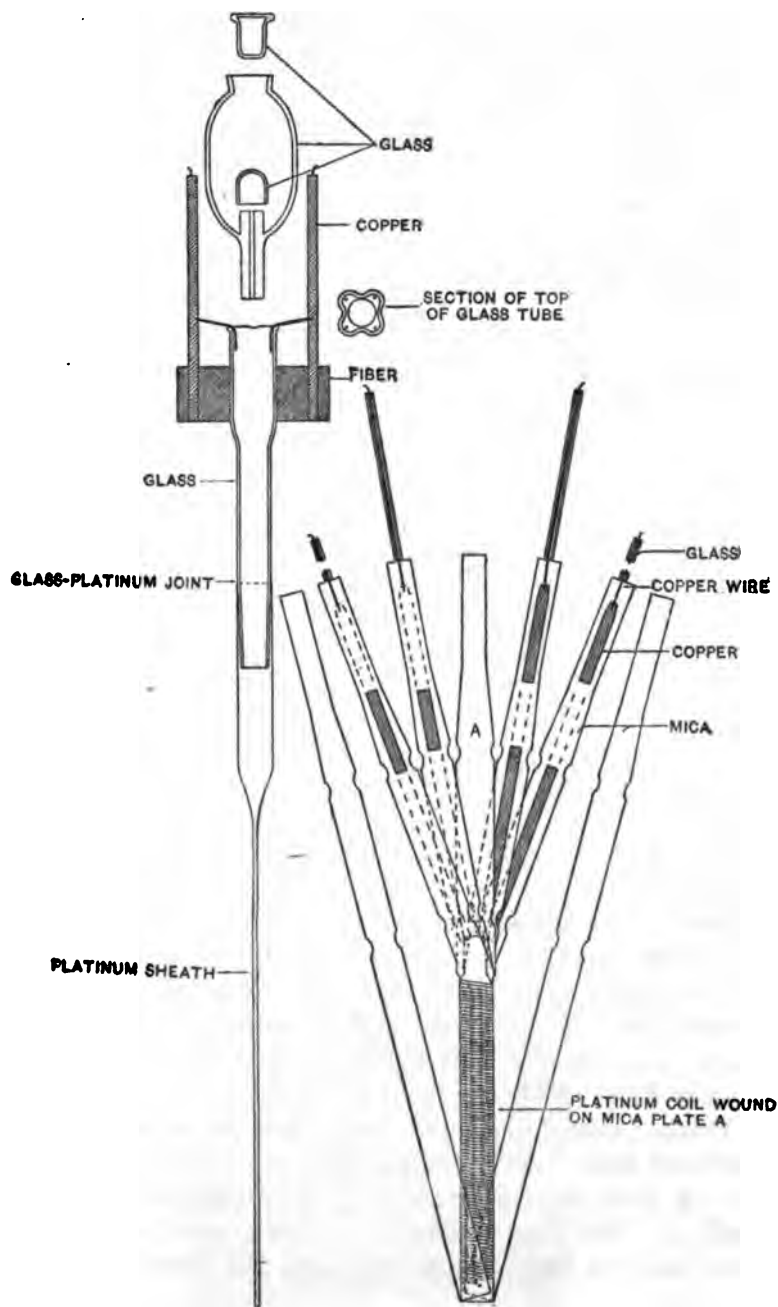


FIG. 5.—Diagrammatic sketch of parts of thermometer, separated to show construction.

greatly improved over that form. In these later thermometers the resistance coils are of the purest platinum wire 0.1 mm in diameter, wound on a flat mica strip. The coil thus formed is about 8 mm broad, 8 cm long, and between 0.7 and 0.8 mm thick, including the sheath. The leads to this coil are of thin copper and compensated for heat conduction as described in the above-mentioned papers. Instead of four leads, arranged as in the Callendar form of resistance thermometer, these later thermometers are of the Siemens form, made with three or four leads (two of each form), with the leads connected in such a way that one of them is in the battery circuit of the bridge while the coil and one lead are in one arm of the bridge and the remaining lead in the adjacent arm. (See Fig. 7.) When four leads are provided, one of them is simply

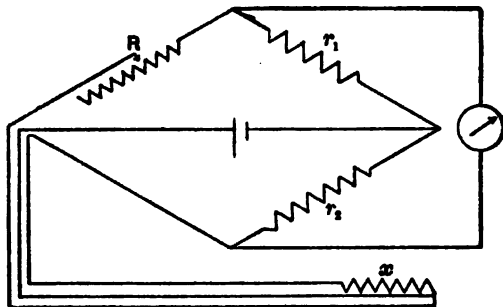


FIG. 7.—Wheatstone bridge and thermometer circuit

left open when the thermometer is used with the Wheatstone bridge. The advantage of four leads connected in this way is that such a thermometer can be used with the Wheatstone bridge, a Kelvin double bridge, or a potentiometer, interchangeably.

The coils and leads of these thermometers are inclosed in thin tubes (two of the thermometers with platinum tubes and two with silver) 7 mm in diameter and 18 cm long, which are flattened except at the upper end. At this end they are slipped over previously platinized glass tubes and soldered in place. The glass tubes end above in a chamber which contains P_2O_5 to keep the coil free from moisture. The construction of these thermometers is shown in Figs. 5 and 6.

(b) *Bridge*.—The bridge used with these thermometers is one designed and built especially for resistance thermometer measurements. A brief description of it is given in the paper above referred to. The later observations were made with a bridge recently built on the same general lines but with a number of



FIG. 6. -*New form of calorimetric resistance thermometers*

decided improvements. This bridge will be described in a future publication. The galvanometer which has been used is a Weston instrument of the moving coil type having a sensibility of 5 mm per microvolt when connected in series with the resistance (45 ohms) necessary for critical damping. The complete period is five seconds.

(c) *Chronograph*.—For observing during the period when the temperature is rising rapidly it has often been found convenient to use a chronograph. The instrument used is of the tape form in which the tape has a speed of 1 cm per second. The same chrono-

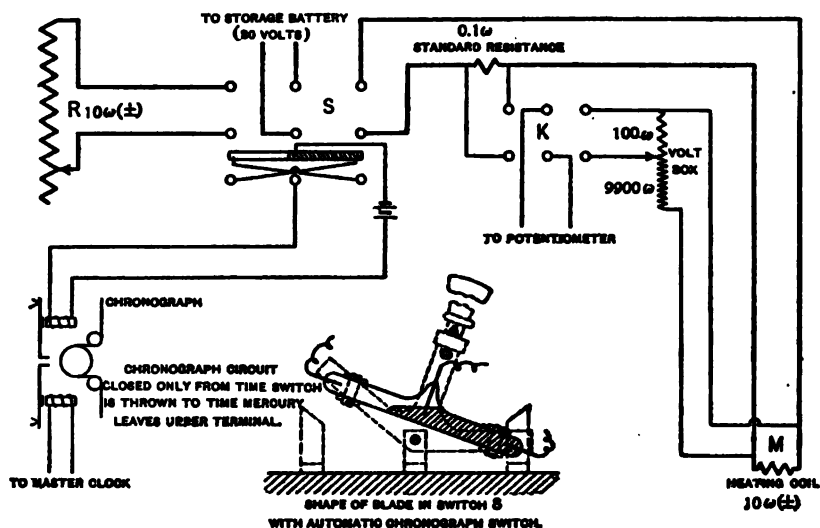


FIG. 8.—Diagram of circuits for energy measurements

graph was used in the electrical method of calibration, to be described later (Fig. 8).

(d) *Speed regulator*.—With the earlier calorimeter a small friction governor was used to control the speed of the stirrer, but with the later one a constant speed induction motor is used with a speed indicator sensitive to 1 per cent or 2 per cent. The indicator is shown in Fig. 1.

5. Heat Capacity.—The calorimeter here described was built with such care as to the weight and quality of materials that the heat capacity of its metal parts, nearly all pure copper, is known

about as well as the specific heat of pure copper is known. The total value of this heat capacity is less than 1.5 per cent of that of the water which the calorimeter contains. The specific heat of copper has been determined by the substitution of a 5-kg cylinder of electrolytic copper in place of the bomb; also by observations made with a special calorimeter by Dr. D. R. Harper, and which are to be published in another paper. The results of these tests are given below and are probably reliable to within 0.5 per cent.

TABLE 1
Specific Heat of Copper

0°	25°	50°
0.0906	0.0917	0.0928

PART 2

The remainder of this paper deals particularly with the problem, stated at the beginning, of determining the heats of combustion of some organic solids. For the purpose of this determination the calorimeter must be used in connection with some form of calorimetric bomb. This requires, therefore, the determination of the heat capacity of the particular bomb to be used. The heat capacities of four bombs have been determined, but only two of them were used to any extent.

No. 1, of the Kroeker type, is of steel with a cover of bronze and a fixed platinum lining, and was made by Julius Peters, of Berlin. It has a capacity of about 275 cm³. (See Fig. 9, p. 219.)

No. 2 is similar to No. 1 except that it has a lining of porcelain enamel.

No. 3 is of a special cast bronze, spherical in form, with a lining of electrolytically deposited gold, and was made by Henry J. Williams, of Boston. It has a capacity of about 600 cm³.

No. 4 is of steel, made in the form of two hemispheres. It has a removable platinum lining, and was made by the Emerson Instrument Co., of Boston. It has a capacity of about 400 cm³.

VI. METHODS OF EXPRESSING RESULTS

The unit of heat in the cgs. system is generally defined as that quantity of heat which will raise the temperature of the unit mass of water 1°, the mean temperature being either 15° or 20° C; or

as one one-hundredth of the amount of heat required to raise the temperature of unit mass of water from 0° C to 100° C. These define, respectively, the "fifteen degree calorie," the "twenty degree calorie," and the "mean calorie."

Although the 15° calorie and the 20° calorie have each been adopted by many experimenters, the former by perhaps the larger number, several advantages may be urged for the adoption of the 20° calorie. Perhaps the most important of these is the much smaller rate of change in the heat capacity of water at the latter temperature. This heat capacity reaches a minimum at about 30° , and its rate of change with temperature at 20° is only about one-third as great as at 15° . For this reason results can be obtained in the neigh-

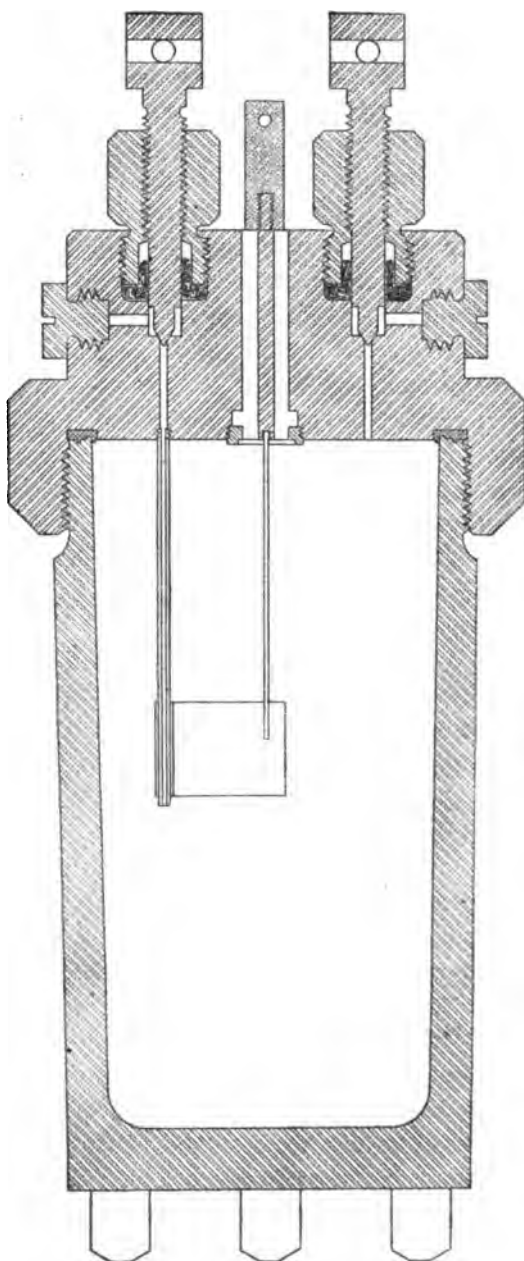


FIG. 9.—Section of bombs, B. S. 6316 and 6216.

borhood of 20° with considerably greater consistency than in the neighborhood of 15° .

Another advantage lies in the fact that 20° is a more convenient working temperature than 15° . In many places the customary laboratory temperature is approximately 20° , while in summer the outside temperature and humidity are such as to make it impossible to use an open calorimeter at 15° without a means of reducing the temperature and humidity of the air. On the other hand, it is usually a very simple matter to maintain a calorimeter at a temperature several degrees above that of the room. Results obtained at 20° can be more accurately expressed in terms of the 20° calorie.

In view of the greater convenience of 20° as a working temperature, smaller rate of variation in the heat capacity of water at this temperature, and the fact that calorimetric observations are commonly made at temperatures near this, it appears desirable to follow what seems to be a growing tendency among experimenters and adopt the 20° calorie as the basis for expressing the results of this investigation.

Although the calorie has been adopted as the primary unit of heat, the extreme precision with which electrical measurements can be made has led to the use of the joule expressed in electric units, as a calorimetric unit. Such use involves the acceptance of a specific value for the ratio J of the joule to the calorie, when results are to be expressed in calories.

The adoption of such secondary units is hardly justifiable unless greater comparative accuracy can be obtained thereby. The present investigation seems to show that this is not true to any considerable extent. It seems, therefore, that the calorie should be adopted for work of this kind, and in this case the incidental values of J , which will be found as shown later, will serve as an excellent check on the other measurements by comparison of these values with those of other observers, taking care that the same numerical values are assigned to the electrical units used.

In view of these considerations it has been decided to express the results of the present investigation directly in terms of the calorie, but in finding the heat capacity of the several bombs, to make the

fullest use of the methods applicable for calibration in terms of the joule.

VII. ELECTRICAL CALIBRATION APPARATUS

The electrical method of calibration consists essentially in supplying a measured amount of energy electrically to the calorimeter, and measuring the temperature rise, with all conditions as nearly as possible those of the experimental work for which the calorimeter is intended. The results of such observations give directly the heat capacity of the calorimeter and its contents, in joules per degree, but to make use of this very accurate method to the fullest extent in determining the heat capacity of a combustion bomb in calories per degree it should be possible to make a determination first with the bomb in place in the calorimeter and then a similar observation with the bomb removed. The removal of the bomb involves a change in conditions respecting both the heat capacity and the form of the temperature-time curve. In order to eliminate these two effects and make the conditions nearly the same in the two cases, the approximate volume and heat capacity of each bomb were determined and for each of the different types a very light copper buoy was made, of such a size that it would displace just enough water in the calorimeter so that, when it was substituted for the bomb and the water level was made the same as with the bomb in place, the total heat capacity of the calorimeter would remain nearly unchanged. The shape and position of the buoy were much the same as of the bomb, so that the conditions of stirring were little affected.

1. **Heating Coils.**—In order to supply energy to the water electrically and not to introduce a large mass of material of uncertain heat capacity, three closed heating coils were built as follows: A strip of "Advance" resistance ribbon, 3 mm wide and about 8 m long, with a resistance of 10 ohms, was wound over thin mica insulation on a cylinder of 0.2 mm copper, then covered with another layer of mica and closed with a second layer of copper 0.1 mm thick, soldered at the edges. One of these coils is 10 cm in diameter. Another is of a diameter to fit closely over either of the two Peter's bombs, covering most of their cylindrical surfaces. The third is about 12 cm in diameter and was built for the calorim-

eter, B. S. 7602. The current and potential leads of the first and second coils are brought out through small glass tubes. These leads branch near the surface of the calorimeter water so that the potential is measured across only that part of the coil which is immersed in the water.

In building the third heating coil it was recognized that if the portion of a current lead adjacent to the jacket is at the jacket temperature and the portion entering the calorimeter is at calorimeter temperature, the potential lead should be connected at such a point that the thermal conductivity between this point and the calorimeter is the same as that between this point and the jacket. To satisfy this condition the leads must be in very good thermal contact with both jacket and calorimeter and the ends next the heating coil must not be appreciably affected by the heating of the coil, otherwise the temperature gradient will depend upon the current in the coil. The above conditions are quite approximately realized by making the leads in the form of wide, flat copper strips insulated with mica, and resting firmly against the upper surface of the jacket, is shown at Q in Fig. 4, by interposing a few centimeters of thin copper ribbon of low resistance between the leads and the resistance ribbon as wound on the coil and by connecting the potential leads at the proper median points.

The form of temperature-time curve, observed when the close-fitting coil is used, is markedly different from that observed when the open coil is used, as may be seen from the figures given later (Fig. 10 a-b). When the open coil is used and a current passed through it for a given time, the temperature of the calorimeter water rises almost linearly until the current is cut off, then very soon reaches a steady condition. When the close-fitting coil is used, however, the temperature rises less rapidly at first, showing that much of the heat is being taken up by the metal of the bomb, and after the current has been cut off the temperature continues to rise for a considerable time while the metal of the bomb is losing its heat to the water. The form of this curve is much the same as that observed when a charge of combustible is burned within the bomb. The curve obtained with the copper buoy in place of the bomb is almost identical with that obtained with

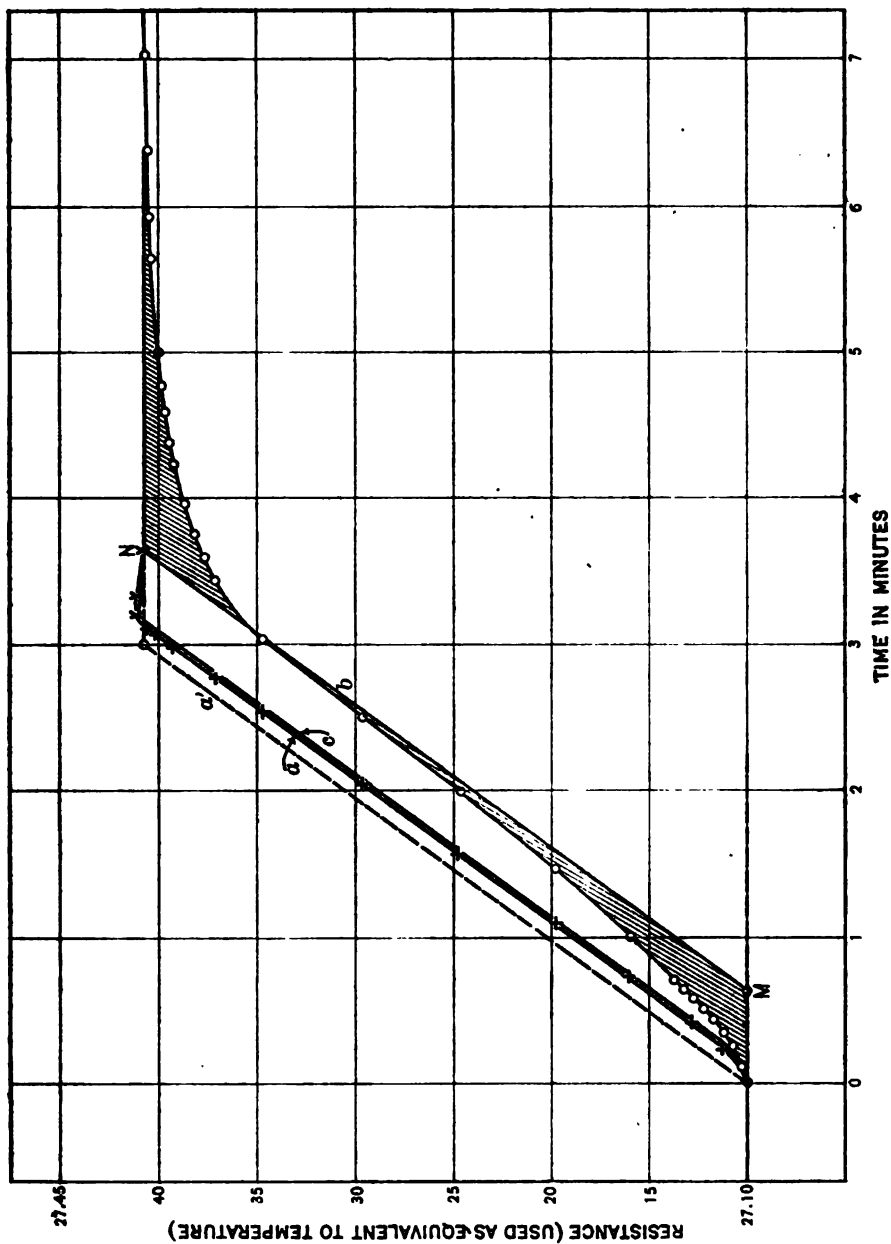


FIG. 10.—Typical time-temperature curves for electrical calibrations.

the open coil and the bomb, so that for comparisons with and without the bomb the open coil is the better. It is interesting to note, later, that the results obtained with the open and the close-fitting coils and the bomb are in perfect agreement with each other, though the cooling corrections to be applied in the two cases are very different.

2. Electrical Measurements.—The electrical measurements consisted of a determination of temperature by means of an accurate resistance thermometer used in connection with the special resistance bridge, referred to in the earlier part of this paper, and a determination of current and voltage during the time when the heating current was flowing through the calorimeter heating coil. The arrangement of the thermometer and bridge circuits is shown in Fig. 7. Since measurements must be made with a changing temperature the method used was to set the bridge resistance to a given value and note the time when the galvanometer deflection became zero. The arrangement of circuits for measurement of current and voltage and for recording the time is shown in Fig. 8. The adjustable resistance R was made equal to the resistance of the heating coil in the calorimeter, so that on throwing the quick-break switch S no change was made in the current taken from the storage battery, and by using a battery which was partly discharged it was possible to keep the current constant to well within 0.01 per cent for the time (usually 3 to 5 minutes) during which it was flowing through the heating coil. Measurements of current and voltage were taken alternately by throwing the switch K , which connected the potentiometer with either the standard 0.1 ohm or the volt box. All the resistances in the bridge, potentiometer, and volt box, and the standard 0.1 ohm were often calibrated and were accurate to 2 parts in 100 000.

For the measurement of time the tape chronograph was used in connection with the Riefler clock kept by the division of weights and measures. By the arrangement of switches shown in Fig. 8 the operation of throwing the switch S automatically closed the chronograph circuit. The chronograph tape traveled about 1 cm per second, so that times could be read easily to 0.01 or 0.02 second. The quick-break switch S , which operates the main current circuit and the chronograph circuit, is so made that there is

not more than 1 or 2 mm of motion between the opening of the circuit on one side and the closing of the circuit on the other side. The time required to move this distance evidently enters as an error in the chronograph time interval, but since this error could not exceed a few thousandths of a second or a part in 100 000 it was neglected.

S is a three-pole switch with a glass tube partly filled with mercury mounted upon it in such a way that while the third pole serves to close the chronograph circuit on either side, the motion of the mercury opens the circuit immediately afterward, allowing only time for the chronograph to operate, and leaving the connections right for the next throw of the switch.

VIII. HEAT CAPACITY DETERMINATION

The method adopted requires a comparison of two sets of observations entirely similar except for the interchange of bomb and buoy. The procedure need be described for only one of the sets—e. g., when the bomb is used.

1. *Procedure.*—A suitable amount of distilled water, at a temperature a few degrees lower than that of the room, was poured into the calorimeter and weighed to tenths of a gram. The calorimeter was put into position in the jacket, the temperature of which had been lowered to within 2° or 3° of that of the calorimeter. The bomb was lowered into the calorimeter and brought the level of the water up to within 1 cm of the top. Different amounts of water were used with different bombs so that the upper surface of the water was always at nearly the same level. The heating coil M and the cover were put in place, 0.3 cc of oil was dropped on the surface of the water which was exposed in the openings of the cover, the jacket cover was turned into position, and the stirrer connected.

The main observations required two observers and can be divided into initial, middle, and final periods. In the initial period observations were made with the resistance thermometer. First, a series of four or five observations were made of the time when the galvanometer deflection was zero for settings on the bridge differing by 0.0001 or 0.0002 ohm, corresponding to approximately

0°001 or 0°002. Then after from five to eight minutes another similar series was taken, usually comprising more observations.

The middle period began at the end of this series when the second observer closed the switch S, Fig. 8, and began taking observation of current and voltage, as described on page 224 et seq. At the same time the observer at the bridge recorded on the chronograph tape the times when the galvanometer deflection became zero for various settings of the bridge at intervals of resistance corresponding to temperature differences of from 0°2 to 0°5, according to the rate of temperature rise. During this period the sensibility of the galvanometer was reduced and determined in terms of resistance so that galvanometer deflections could be observed and used to plot additional points on the time-resistance curve when desired. At other times the temperature observations during the middle period were made with a thermocouple, with junctions on the calorimeter and jacket, and connected directly to the galvanometer. At the end of 2, 3, or 4 minutes, as the case might be, the switch S was again thrown, cutting off the current from the heating coil and automatically recording the time on the chronograph. For convenience this switch was always thrown both on and off at an even minute—i. e., at the same second—so that any possible error in the contact device of the clock, such as eccentricity of the seconds wheel, was eliminated. A watch was used by the observer to indicate the second on which the switch was to be thrown, and to record the time of observations during the initial and final periods.

The final period may be considered as beginning when the rate of temperature change has become sensibly constant, as shown by equal time intervals between observations of equal resistance changes. When the rate had become sensibly constant, a series of observations, like those in the initial period, were recorded, and after several minutes another series. As the rate was always slow the time in these observations need seldom be known to better than one second and the watch was sufficiently accurate. These observations serve to determine the initial and final cooling rate.

After finishing a series of observations of this kind the temperature of the jacket was raised the same amount as the temperature

of the calorimeter had been raised, and another similar series of observations was taken. In this way with a single filling and adjustment of the calorimeter as many as five observations were made. The whole set of observations was again carried out with all the conditions as nearly as possible the same, except for the substitution of the thin copper buoy in place of the bomb, and the two series of observations thus obtained served for a calculation of the heat capacity of the bomb. This is virtually a comparison of the bomb with a mass of water which is very nearly its equivalent in heat capacity.

2. Form of Records.—Table 2 shows the form in which the observations were made and the computation carried out.

The original record includes under "Amperes" and "Volts" the potentiometer readings corresponding to current and voltage, and under "on" and "off" the times of throwing on and off the heating current. The exact times are entered from the chronograph record. Under "Time" and "Resistance" are recorded the times and corresponding resistance readings on the bridge. During the middle period the bridge readings may often be omitted. The times (when required) during the middle period may be entered later from the chronograph record or may be observed with a watch. The weight of water used and other data are entered under the proper headings.

TABLE 2
Department of Commerce
BUREAU OF STANDARDS
Washington

Observer HCD
Computed by HCD

Date Jan. 27, 1913
Expt. No. 4

WATER-EQUIVALENT RECORD

		(n_1)	(n_2)	TIME	DIF.	RESISTANCE	NOTES
t_n 2-52-33	dR	.0088	.00151	2-44-10	12	28.22700	Bridge BS 7481 at 30°C.
t_m 2-55-31	dt	503	960	22	9	20	Calib. of 11-16-12
dt 2-58 -178	$\frac{dn}{dt}$	.001749	.00157	31	13	40	Ratio 100 R.
r_1 .001733	Cor.	.00016	.00003	44	12	60	Therm. Pt 4
r_2 dt +.00308	r	.001733	.00160	56		80	5 mill'amps.
R_1 28.23580	s	.0037					
R_1 cor .23888	R_o			2-51-46	12	28.23500	
Potentiometer No. 1665	Cell No. 1506			58	13	20	
Volt Box No. 8325	Std. Res. No. 4997			52-11	11	40	
Temp. 1995	Temp. 1996			22	11	60	
				33		80	
49.358		4.9380					
56		75					
53				2-53-03		28.24	
				08		.25	
				38		.30	
Mean 49.356	Mean 4.9378			54-07		.35	
Pot. Cor. +1	Pot. Cor. +1			37		.40	
Vib. fctr. 0	Res. Std.			55-06		.45	
	Vit. bz. cur.	-90		35		.50	
				56-04		.55	
Volts 49.357	Ampere 4.9289			35		.60	
Resistance 10.0138	Power 243276			57-03		.65	
				34		.70	
on 2-52-51.28	Time 300.01	Energy 72985		52		.73	
off 57-51.29							
t_n 3-02-00	Calorimeter No. 7602						
t_m 2-55-31	Bomb " 6316 ₁			2-59-33		28.74350	
dt 6-29 -389	Total Wt. 3500.0			3-00-02		40	
r_1 .00160	Tare 409.3			01-00		33	
r_2 dt .00062	3090.7			2-00		26	
R_1 28.74326	Vac. 3.2 _g			3-00		17	
R_1 Cor. .74388	Cor. Mass 3094.0H ₂ O			4-00		05	
R_1 Cor. .23888							
diff. .50500	Total H ₂ O equivalent of			3-16-00		.74192	
Bdg. 00	Cal. Therm. Cell etc. at			17-00		83	
	32°-53.9 Cal. ϕ 225.4 J			18-00		75	
dR .50500							
K 1.01035	ROOM TEMP.	JACKET					
d θ 591023	Therm.	Therm.					
Equiv. 14306 J	Time Temp.	Time Temp.					
Mn. Temp. 32°:1	2-46 21.3	2-46 35.5					
	3-06 .4	3-06 .5					

The resistances were read directly on the bridge; the coil corrections being small were entered under "Bdg" during computation. The time intervals between successive readings under "Dif." serve to indicate when the cooling rate has become uniform and to compute a correction to the time which corresponds to any chosen resistance.¹²

3. Computation.—Observations with the resistance thermometer, more particularly during the middle period, are more conveniently made at even resistances than at even time intervals. For this reason formulae such as Pfaundlers are not conveniently applied. A graphical method has been developed which, though somewhat laborious when worked out completely, leads to a very short and simple practical method of correcting for heat transfer, applicable in both electrical calibration and combustion observations with errors so small as to be negligible even in work of high precision.

Fig. 10 shows typical curves plotted with times as abscissae and resistances (instead of temperatures)¹³ as ordinates. In this figure a' represents the curve which would be found, provided the heat

¹² In a series of resistance-time observations, as above, it is often desirable to find a corrected value for one of the observations rather than a mean value for several of them. A series of time observations is made, which in general have a constant difference—i. e., a linear variation—but which show fortuitous errors of observation. It is desired to find the best value of time corresponding to the resistance measured immediately at the end of the initial period since by using this observation the cooling correction can be made smaller than if a mean were taken of a number of observations. The corrected value of the time can be conveniently computed from variations of the quantities in the column "Dif." as follows:

Let a_1, a_2, a_3 , etc., be a series of observations such that β is the mean of the differences $a_2 - a_1, a_3 - a_2$, etc., any observation $a_n = a_{n-1} + \beta + x_{n-1}$ where x is the departure of the individual difference $a_n - a_{n-1}$ from the mean difference β .

The corrected value for a_1 may be written as a' where

$$(1) \quad a' = \{a_1 + (a_2 - \beta) + (a_3 - 2\beta) + (a_4 - 3\beta) + \dots + [a_n - (n-1)\beta]\} + n = \{a_1 + a_2 + a_3 + \dots + a_n - \beta[1+2+3+\dots+(n-1)]\} + n$$

But the above series of a 's is made up as follows:

$$\begin{aligned} a_1 &= a_1 \\ a_2 &= a_1 + \beta - x_1 \\ a_3 &= a_1 + 2\beta - x_1 - x_2 \\ a_n &= a_1 + (n-1)\beta - x_1 - x_2 - \dots - x_{n-1} \end{aligned}$$

Substituting these values in (1) and simplifying

$$(2) \quad a' = a_1 - (1/n)\{(n-1)x_1 + (n-2)x_2 + \dots + x_{n-1}\}$$

This formula is usually applied for $n=5$, and the value of β used to get the x 's is from the mean of as many differences "Dif." as seem to be regular. The computation of a correction by this means can be made mentally in a few seconds after finding β .

¹³ Resistances may be used in plotting the curves since the resistance-temperature relation is very nearly linear, and Newton's law of cooling may be assumed for resistances in the same way as for temperatures.

from the heating coil was instantly distributed to the water and provided the thermometric system had no time lag; *a* represents actual observations when the calorimeter was heated electrically with an open heating coil and with the calorimetric bomb in place; *c* represents observations taken at the same time with the differential thermometer in the air space between the calorimeter and the jacket; *b* represents observations taken when the calorimeter was heated by means of the heating coil which fitted closely the surface of the bomb. It should be noted that the curve *c* is displaced from *a* by two and one-half seconds. A series of 10 observations of this displacement, taken with various rates of temperature rise, all gave values of between two and three seconds.

Fig. 11 is a characteristic curve observed when a charge of combustible was burned in the bomb. The ordinates are resistances, as in the preceding figure. This figure is so drawn as to illustrate the method of computing cooling corrections, discussed below.

$$\text{The cooling correction } A = \alpha \int_{t_1}^{t_2} (\theta - \theta_0) dt$$

where

α = cooling constant of the calorimeter.

θ = temperature; θ_1 , θ_0 , θ_2 , respectively initial, convergence, and final temperatures.

t = time; t_1 and t_2 respectively initial and final times.

A time t_m may be found such that

$$\begin{aligned} r_1(t_m - t_1) + r_2(t_2 - t_m) &= \alpha \int_{t_1}^{t_2} (\theta - \theta_0) dt \\ (1) \quad &= \alpha \int_{t_1}^{t_m} (\theta - \theta_0) dt + \alpha \int_{t_m}^{t_2} (\theta - \theta_0) dt \end{aligned}$$

where

$$r_1 = \alpha(\theta_1 - \theta_0)$$

$$r_2 = \alpha(\theta_2 - \theta_0)$$

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¹⁴It may be shown that this is true, independently of the form of the curve, as, for instance, when the temperature rises above the final temperature θ_0 , as in Fig. 10, *a*. If the line MN in Fig. 10 is so drawn that the shaded areas are equal, the middle point of this line may be taken as t_m .

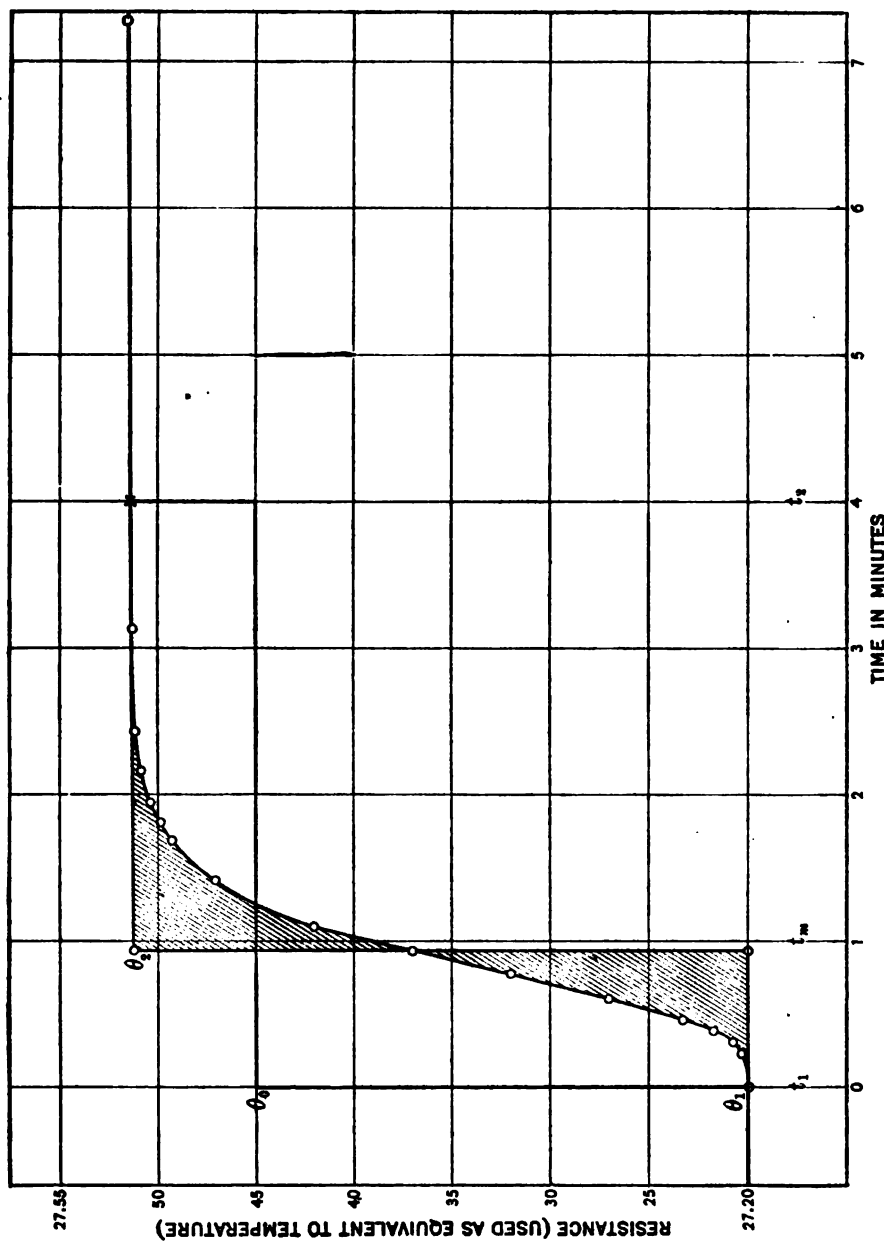


FIG. 11.—Typical time-temperature curve for combustion observations

The geometry of Fig. 11 suggests that the above condition (1) will be satisfied if t_m is so chosen that the shaded areas between the curve and the lines θ_1 and θ_2 are equal on either side of it.¹⁵

$$(3) \quad \text{that is } -\alpha \int_{t_1}^{t_m} (\theta_1 - \theta) dt + \alpha \int_{t_m}^{t_2} (\theta_2 - \theta) dt = 0$$

Adding (2) and (3)

$$\alpha(\theta_1 - \theta_0)(t_m - t_1) + \alpha(\theta_2 - \theta_0)(t_2 - t_m) = A$$

or

$$A = r_1(t_m - t_1) + r_2(t_2 - t_m)$$

which is a very convenient form to use.

It is only necessary to multiply the initial cooling rate by the time $(t_m - t_1)$ and add the product to the initial temperature, and multiply the final rate by $(t_2 - t_m)$ and add the product to the observed final temperature. The difference of the two temperatures thus corrected gives the true temperature rise corrected for the effect of heat transfer between calorimeter and surroundings.

If a curve is plotted it is a simple matter to locate t_m , but experience shows that for electrical calibrations (with the open coil) the position of t_m with respect to the beginning and ending times is, for a sufficient rate of stirring, remarkably constant; in fact, for scores of electrical calibrations its position has never varied more than 2 seconds from the mean value, this mean being 8 seconds later than the middle point of the heating period. An error of 2 seconds would affect the result by about 6 parts in 100 000. In combustion experiments the agreement is not so good, as t_m depends both upon the time required for the charge to ignite after closing the switch and upon the total rise of temperature. But it was noted that the position of t_m with reference to the temperature for combustion observations was remarkably constant, the line t_m crossing the temperature-time curve always

¹⁵ The factors r_1 and r_2 are the rates of cooling at times t_1 and t_2 , not the rates computed from observations covering periods of time respectively preceding t_1 and following t_2 .

If θ_1' be the temperature at a time t_1' earlier than t_1 , the observed rate r_1' will be $(\theta_1 - \theta_1') + (t_1 - t_1')$ and the rate at time t_1 may be found from this by means of the relation $r_1 = r_1' \left\{ 1 - \alpha \frac{\theta_1 - \theta_1'}{r_1'} \right\}$ which simply assumes that the change in rate is proportional to the change in temperature. The final rate r is found in the same way.

at nearly the same relative position. This fact suggested the following calculation, which is given in this connection although it applies more particularly to combustion observations.

If the heat generated were all distributed instantly to the walls of the bomb, the rise of temperature of the water would follow very nearly an exponential law corresponding to the cooling constant of the bomb in water—i. e., $\theta = 1 - e^{-kt}$ —for unit rise of temperature from an initial temperature of 0° . As a matter of fact, the temperature does very nearly follow such a law beyond the first few seconds after firing. Assuming $\theta = 1 - e^{-kt}$, t_m may be found in terms of θ .

For convenience, assume $\theta_1 = 0$, $\theta_0 = 0$, $\theta_2 = 1$, then for t_m to satisfy the condition of equal areas as given above:

$$\int_0^{t_m} [1 - e^{-kt}] dt = \int_{t_m}^{\infty} [1 - (1 - e^{-kt})] dt$$

integrating and simplifying

$$t_m = \frac{1}{k}$$

and substituting to get the value of θ , i. e., (θ_m) corresponding to t_m

$$\theta_m = 1 - e^{-\frac{K}{K}} = 0.63$$

Thus, if the time is observed when the temperature rise has reached 0.63 of its final value, this time may be used as t_m . A large number of observations for which the curves have been plotted give 0.57 to 0.62, always slightly less than that for the exponential curve, due, probably, to the fact that the temperature rise does not begin as soon as required by the assumption. (When gases are burned in the bomb the observed value for t_m is very nearly the same as the computed value, viz, 0.63.)

If the figure 0.60 were used in all these observations, the error introduced would in no case exceed 1 in 10 000.

When the total rise in temperature to be expected is approximately known it is only necessary to observe the time when 0.6 of that rise has occurred and to use this time as t_m . The degree of

approximation which can be permitted must be determined for any given class of experiments.

The above method of computing the cooling correction is plainly independent of the units used for plotting the ordinates of the curve and is therefore applicable directly to observations taken with the differential thermometer or thermocouple in terms of galvanometer deflection, provided the deflection is nearly a linear function of the temperature difference.

The observations for the middle period have always been made with the thermometer in the calorimeter, and not with the differential thermometer, described on page 207. The data necessary for correcting these observations to a basis of the differential thermometer were obtained from a series of comparisons between observations made with it and the inside thermometer under conditions similar to the above. The curves plotted from these observations were almost identical with the curve Fig. 10, *a*, except that they were displaced on the average $10\frac{1}{2}$ seconds from the ideal curve AB instead of 8 seconds, as is the average for curves taken with the thermometer in the calorimeter. From this it is concluded that a correction of $2\frac{1}{2}$ seconds should be applied to all observations with the thermometer in the calorimeter. Under like conditions the displacement observed very seldom differs from the mean displacement of 8 seconds by more than 1 second, which corresponds to an error of about 0.00003 (3 parts in 100 000) in the observed temperature difference.

The computation of results on this observation sheet can be best explained by indicating the entries under each heading.

Under T_R and under R , five lines below, are entered, respectively, the corrected time and the corresponding resistance observed immediately before throwing on the heating current. The device for correcting the observation of time is explained in note 12.

Under t_m is entered the time corresponding to the vertical line in Fig. 10. In this case t_m is 10 seconds after the middle of the heating period.

dt is $t_m - t_R$.

r is the cooling rate determined from observations.

rdt is the product as indicated.

R_1 cor. is the sum of $r dt$ and R the resistance which would have been observed at time t_m if the actual cooling conditions had been operative without any energy supply from the heating coil.

For the computation of the cooling rates r_1 and r_2 under dR and dt are entered differences in resistance and in time between a pair of observations as far apart as possible during the initial period. One of these observations is always that recorded under t_2 and R .

$\frac{dR}{dt}$ is the apparent cooling rate.

"Cor." is a correction equal to $\alpha \frac{dR}{2}$, and is applied to reduce the cooling rate $\frac{dR}{dt}$ to the correct value r_1 which it would have at the time t_2 , i. e., for resistance R_1 .

The "amperes" and "volts" are potentiometer readings with the indicated corrections applied. "Resistance" is the observed resistance of the heating coil entered as a check on the observations.

The following headings t_2 etc., are like those at the top of the page except that they apply to the final period. t_m is the same in both cases, and R_1 cor. is the resistance for the time t_m if all the energy had been supplied before that, and existing cooling conditions had held.

R_1 is entered from above, dR is the corrected change in resistance, and K is a term depending upon the constants of the resistance thermometer, which reduces the observed difference of resistance to difference of temperature $d\theta$. The method of computing the table from which this term is obtained is described in Bureau of Standards Reprint No. 200.

The corrected weight of water and the calculated heat capacity of the fixed part of the calorimeter are given below. To find the heat capacity of the bomb it is only necessary to compare the results of observations including the bomb with those without it. If W is the heat capacity of the calorimeter, heating coil, and water, exclusive of the bomb, B is the heat capacity of the bomb and K is that of the displacement buoy and the additional water used when the bomb is not in the calorimeter; the two equations given

below give the value of $K - B$ from which B can be determined by using an approximate value of J , since $K - B$ is made small.

$$W + K = \left(\frac{A_1 V_1 T_1}{\theta_1 J} \right)$$

$$W + B = \left(\frac{A_2 V_2 T_2}{\theta_2 J} \right)$$

This method of determining the heat capacity of the bomb alone does not require an accurate knowledge of the heat capacity of the fixed parts of the calorimeter nor of the electric heating element used, and the accuracy attainable is limited only by the precision of the measurements.

An accurate knowledge of the heat capacity of the calorimeter used for combustion experiments (not necessarily the same one as is used for determining the heat capacity of the bomb) must, however, be accurately known in order to express the results in calories. If, in addition to this, the heat capacity of the electric heating element is known, the former of the above equations also gives a value for J , the equivalent of the calorie in electrical units.

The following series of results from observations dated January 27 and January 28, 1913, is representative. Observed joules per degree for the calorimeter with 3093.8 g water (corrected to vacuo), heating coil 7602 and bomb 6316₁,

TABLE 3.

Temp.	15°	20°	25°	30°	35°
Joules.	14317	14309	14307	14306	14305

Observed joules per degree for the calorimeter with 3368.2 g of water (corrected to vacuo), heating coil and displacement buoy of copper equivalent to 4.1 g of water,

TABLE 4

Temp.	15°	20°	25°	30°	35°
Joules.	14334	14322	14317	14315	14314

The heat capacity of the bomb at each of the following temperatures is found from these observations to be equivalent to that of the following masses of water at the same temperatures.

TABLE 5

Temp.	15°	20°	25°	30°	35°
Mass.	274.7	275.7	276.3	276.6	276.7

Or in terms of 20° calories, using the variation in the heat capacity of water, as found from this set of observations,

TABLE 6

Temperature	15°	20°	25°	30°	35°
Specific heat of water.....	1.0009 ₁	1.0000 ₀	0.9994 ₂	0.9991 ₃	0.9991 ₁
Heat capacity of bomb.....	275.0	275.7	276.2	276.4	276.5

The value of J computed from this observation (taking the heat capacity of the calorimeter (p. 240) as 175.5 joules at 15°, and 176.8 joules at 35° of the coil (p. 242) as 47.8 joules, and of the buoy (p. 242) 17.1 joules, and of the 10 drops of oil used to prevent evaporation as 0.8 joule) is 4.181 joules per 20° calorie on the basis of the present electrical units.

The heat capacities of the bombs, particularly of 6316₁, have been determined at various times, the weights being somewhat variable on account of the wearing away of the lead washer used in the cover of the bomb.

A series of observations in 1910, in the earlier calorimeter, gives the following results:

TABLE 7

Bomb	Observations	Temperature			
		15°	20°	25°	30°
6316.....	80	272.7	274.9	276.3	276.7
6316.....	29	272.9	275.1	276.5	277.0
6428.....	57		401.9	403.3	404.5
Em. 549.....	5		402.4	405.0	406.7

A recent series of 15 observations in calorimeter No. 7602, with all the factors very carefully redetermined, gave the following results:

TABLE 8

Temp.	15°	20°	25°	30°
Bomb 63161	275.0	275.8	276.2	276.4

in terms of 20° calories at the temperatures given.

4. Accuracy of the Various Measurements.—The measurements of time were made to an accuracy of about 1 part in 20 000; of current, voltage, and weight to an accuracy of better than 3 parts in 100 000. The potentiometer, volt box, and standard 0.1 ohm have been tested at frequent intervals during the investigation.

The computations of heat capacity of the metal parts of the calorimeter aside from the bomb involve an uncertainty, mainly in the specific heat of copper, which uncertainty should amount to less than 1 part in 10 000 of the entire heat capacity. An error in this would affect all results to the same proportional extent.

The measurement of temperature enters into both the observed temperature interval and the temperature-time curve from which the cooling correction is computed. In fixing the temperatures (resistances) during the initial and final periods the error of the thermometer probably does not exceed 1 part in 10 000 of the interval measured.

The four thermometers built for these investigations and described in Reprint No. 200 were calibrated with great care by comparison with some of the primary standards of the Bureau of Standards in the same manner as were the thermometers described in Reprint No. 68, from the Bulletin of the Bureau of Standards. These four thermometers were also compared in 1910 with the two thermometers previously described in Reprint No. 68 and were finally calibrated by means of observations in sodium sulphate in the manner there recommended. The three methods are in agreement to within 0.002 in 50°. Many later observations have confirmed these results to this order of accuracy. The one thermometer of the four which showed the greatest constancy is designated as Pt. 4, and has been used for most of this investigation. The resistance of this thermometer in ice has apparently not changed by 1 part in 100 000 during three years.

The constants of this thermometer are as follows:

$$R_0 = 25.1818, \quad F.I. = 9.8525, \quad \delta = 1.48$$

All four of these thermometers have been intercompared and they

agree to within 1 part in 10 000 in defining any temperature interval between 0° and 100° .

The effect of errors in temperature measurement during the middle period on the cooling correction is very small since an error of 1 second in the position of the entire resistance-time curve involves an error of only 3 parts in 100 000, and it is an easy matter to observe any point on the curve with greater accuracy than 1 second. Errors in the determination of the cooling rates can only be determined from a study of the values found for the cooling constant from various observations.

The accuracy required in these observations is not high, since the total cooling correction ranges from 2 parts in 1000 to zero for combustion observations, where the final temperature may be from 0.3° to 0.5° above the equilibrium temperature. This procedure does not entirely eliminate the evaporation and condensation of water (see p. 195), and it is only justified by the observed fact that the rate of evaporation from the covered and oil-sealed surface of the calorimeter is negligibly small under these conditions.

5. Cooling Constant.—The observed cooling rate of the calorimeter at any time is the sum of 3 parts, first, the rate of the calorimeter proper represented by its cooling constant in degrees per second per degree difference in temperature between the calorimeter and the jacket; second, the rate due to energy supplied by the stirrer; and third, that due to heat conducted by thermometer leads, firing leads, etc., between the calorimeter and the space outside of the jacket. This latter part could be eliminated if it were practicable to secure sufficiently good thermal contact between these leads and the jacket.

When the jacket temperature remains constant and the cooling constant of the calorimeter is computed from the difference in rates before and after a combustion, divided by the change in temperature, the second and third factors are eliminated. A series of values taken from one month's combustion observations at a mean temperature of 25° gives 0.0000339, with a mean variation of 0.0000003 and a maximum variation of 0.0000007. Comparison of about 100 values of this constant obtained at temperatures ranging from 15° to 45° shows a change of about 0.6 per cent per

degree, the constant increasing with the temperature. For a given calorimeter temperature, however, the cooling constant is independent of the difference of temperature between calorimeter and jacket to within the limits of observation (1 per cent or 2 per cent), for differences up to 5° .

However, when observations are made by the "adiabatic" method, as described later, it is necessary to know the magnitude of the stirring and lead conduction effects. These have been determined at several different times. The stirrer running at its normal speed of 300 rpm, causes a rise in temperature of 0.0000040 per second, which corresponds to 0.057 watt, an amount of energy very much less than is usually dissipated in stirring, yet the rate of stirring is entirely sufficient.

The rate due to lead conduction is 0.0000004 per second per degree difference in temperature between the jacket and the room. This corresponds to 0.006 watt.

6. Heat Capacity of Fixed Portions of the Calorimeter.—The various materials entering into the construction of the calorimeter, heating coils, and displacement buoys, together with their assumed specific heats and calculated heat capacity, are discussed below.

The calorimeter proper, including the calorimetric vessel, the cover above the stirrer, the stirrer and shaft, the main cover, and the immersed part of the thermometer, is made up of the following:

TABLE 9

	Weight	Specific heat		Heat capacity—	
		At 15°	At 35°	At 15°	At 35°
	g				
Copper	420.8	0.0920	0.0927	38.71	38.99
Solder	2.7	.05		.13	.13
Steel	3.6	.10		.36	.36
Platinum	9.6	.032		.31	.31
Gold	.3	.031		.01	.01
Mica	1.0	.208		.21	.21
Glass	2.0	.20		.40	.40
Nickel	14.8	.11		1.65	1.65
Hard rubber				.20	.20
Total				41.9	42.2

The two displacement buoys made to displace, respectively, the Williams and the Peters bombs are of copper and have the following constants:

TABLE 10

Volume, 700 cc; heat capacity, 6.3 g

Volume, 360 cc; heat capacity, 4.1 g

7. **Heat Capacity of the Heating Coils.**—The heat capacity of each of the heating coils used was computed from the weight of copper, mica, constantan, and solder, but as the specific heat of mica in particular was uncertain and rather large, a direct determination of the heat capacity of the two coils *K* and 7602 was undertaken. For this purpose the coils were successively supported within the calorimeter jacket surrounded by air only, with the leads connected as usual. A copper-constantan thermocouple with flat contact plates, insulated with thin mica strips, was arranged with one terminal on the inner surface of the jacket and the other on the surface of the coil. The cooling constant for the coil in this position was determined by two methods: First, by heating the coil several degrees above the temperature of the jacket, then allowing it to cool with no heat supplied, and plotting the observed temperature difference between coil and jacket against time; from these curves the cooling constant can be computed; second, by measuring the energy required to maintain a given constant difference of temperature between coil and jacket, from which the cooling constant is found directly. These two methods gave concordant results for each coil. The heat capacities were then determined by heating the coils electrically by successive steps of about 1° , while maintaining the jacket temperature nearly equal to the rising temperature of the coil. The total cooling corrections were thus made very small. Temperatures of the jacket were measured and those of the coils obtained from the same by differences as shown by the thermocouple.

The heat capacity of a portion of the air in the jacket evidently must be considered as included in the observed heat capacity of the coil. The assumption was made that heat was transmitted to the air equally by all the surface exposed within the jacket. On this assumption the amount to be subtracted from the observed heat capacity of the coils would bear to the heat capacity of all

the air contained in the jacket the ratio of the total superficial area of the coil to that of the inner surface of the jacket plus that of the coil. Five determinations of the heat capacity of coil 7602 each gave 47.8 joules or 11.4 calories, an agreement entirely fortuitous, as the observations were not such as to give this precision. For coil K the results were less concordant, giving from 48.3 to 49.1 joules per degree, the mean being 48.7 joules or 11.6 calories.

8. Total Heat Capacity of the Calorimeter.—From the foregoing results the total heat capacity in 20° calories of the calorimetric system as used for heats of combustion may be calculated as follows:

TABLE 11

Temperature.....	15°	20°	25°	30°
Calorimeter with cover and thermometer.....	41.9	42.0	42.1	42.2
Bomb (6316).....	275.0	275.8	276.2	276.4
Firing leads.....	.1	.1	.1	.1
Half cubic centimeter water.....	.5	.5	.5	.5
Oxygen, 30 atmospheres pressure.....	2.4	2.4	2.4	2.4
Ten drops oil.....	.2	.2	.2	.2
Charge of combustible.....	.4	.4	.4	.4
Crucible (6 gr. Pt.).....	.2	.2	.2	.2
Standard mass of water at 20° and the equivalent heat capacity at other temperatures.....	3096.5	3094.0	3093.1	3092.9
Total.....	3417.2	3415.6	3415.1	3415.3

The relative heat capacities of water here given are from the calibration experiments in this investigation. The relative specific heat of water at 15° and 30°, as determined by different observers using different methods, differs by as much as 0.2 per cent, and the values here used, being determined under conditions peculiar to this calorimeter, would seem to be most nearly correct for use in determining the heat capacity of the calorimeter for use in combustion observations. These values are, however, a satisfactory mean between those found by other observers.

9. Adiabatic Method.—When energy is supplied to the calorimeter by a constant electric current in a coil of small heat capacity and small time lag the rise of temperature is very nearly linear, and by producing a similar rise of temperature in the jacket by the same means, observations, with very small cooling correc-

tions, may be made as suggested by T. W. Richards. This method, therefore, seems to offer much greater advantages under these circumstances than when the rate of temperature rise changes greatly during the experiment.

A considerable number of observations have been made by this method in the calorimeter No. 7602, which is fitted with an auxiliary stirrer and a heating coil capable of supplying enough energy to heat the jacket at the rate of 1° per minute. The method of taking these observations was similar to that already described except that the small cooling correction was computed from the mean difference in temperature between the calorimeter and the jacket, as observed by means of a thermocouple, the junctions of which were small flat plates, one resting on each of the surfaces and insulated from them by thin strips of mica. The total correction seldom exceeded 1 in 10 000.

In order to discover any systematic difference between the adiabatic and the ordinary method of observation the two methods were often applied alternately in the same series while raising the temperature by steps of 3° or 5° from 10° to 45° .

In the following series of results, dated March 18, 1913, taken from observations on a single filling of the calorimeter, the two methods, the ordinary and the adiabatic, were alternated, and corresponding results are marked a and o.

TABLE 12

Mean temperature	Joules per gram	Method
8°.5	14 290	a
11.5	14 273	o
14.9	¹⁰ 14 257	a
18.0	14 245	o
20.9	14 240	a
24.0	14 238	o
26.9	14 238	a
29.9	14 239	o
32.9	14 239	a
35.9	14 240	o
38.9	14 242	a
42.0	14 245	o
44.9	14 254	a

¹⁰ Not in agreement with other observations taken at this temperature; should be 14 352.

The two methods of observation appear from the second column to be in agreement to about 1 part in 15 000. Many other series of such determinations have failed to indicate any significant systematic difference between the results obtained by the two methods.

IX. COMBUSTION EXPERIMENTS

The three substances, sugar, benzoic acid, and naphthalene were chosen for the first series of experiments because of the fact that they have been widely used and are well adapted for use as standard substances for the calibration of bomb calorimeters. Their heats of combustion have been determined by a number of observers and for sugar and benzoic acid the results are in fair agreement, but for naphthalene the values found by different observers differ by nearly 0.7 per cent.

1. Bombs Used in the Experiments.—The two Peters bombs, the heat capacities of which have been determined, were used for most of the succeeding observations and most of these were with 6316₁. Observations with the Williams bomb showed no significant differences from those with the Peters bombs.

The two Peters bombs are entirely similar except that one is lined with platinum and the other with porcelain enamel. The material is steel for the body of the bomb and bronze for the cover. Details of construction are given in Fig. (9).

2. Materials Used for Combustion Experiments.—The sugar¹⁷ used in these determinations was all from samples prepared by R. F. Jackson, of the Bureau of Standards, and contained less than 0.01 per cent of impurities, including water.

The benzoic acid for the 1910 series was from samples purified by G. E. Morey, of the chemical division of the Bureau of Standards. The original samples were from different sources and the samples used were purified in various ways. All the purified samples were, however, of such a degree of purity or at least of uniformity that various results appear entirely comparable for the different samples, showing no consistent differences greater than the errors of observation.

¹⁷ Bureau of Standards Circular No. 44, p. 83.

The naphthalene for the 1910 series also was prepared by Mr. Morey from samples obtained from different sources and the observations include a series made upon some samples as received, without further purification. The preparation of these materials is the subject of a separate report by Mr. Morey.

Difficulty is experienced in securing pure oxygen, which must be used at a pressure of from 30 to 45 atmospheres for filling the bombs. After considering this problem it was decided to prepare oxygen by the electrolytic process and compress it to a pressure of 100 atmospheres for use. With this object in view an electrolytic generator was designed and built. The generator consisted of a battery of nine cells connected in series and taking a current of about 20 amperes at 120 volts. For compressing the gas a two-stage compressor was designed and built, using mercury for the compressing pistons so that the oxygen during compression came in contact only with mercury and steel. Unfortunately the time required for building this apparatus was so long that it was impossible to have the pure oxygen for the present series of experiments and a supply was obtained commercially which contained only a small amount of nitrogen, amounting in different cylinders to from 0.3 per cent to 0.5 per cent. The remainder of a residue of about 2.5 per cent was found to be argon. The amount of nitric acid formed under like experimental conditions seems to be approximately proportional to the amount of nitrogen contained in the oxygen. The correction to be applied for the heat of formation of the HNO_3 , as determined by titration, was usually about 1 part in 1000, so that the small amount of nitrogen present can hardly have had an appreciable effect on the results, beyond that accounted for by this correction.

3. Order of Procedure.—The required amount of water (total weight in air, of calorimeter and water = 3500 g), was weighed out in the calorimeter and the same placed in the jacket as for a heat capacity observation.

A sample of the combustible of about the desired amount was compressed into a briquette and weighed in the platinum crucible in which it was to be burned. The amount used varied from 0.6 g to over 2 g, depending upon the material. After weighing,

the crucible was placed in the bomb, the cover screwed in place, and the inlet coupled to the oxygen filling system. First the bomb was exhausted to a few centimeters pressure by means of the laboratory vacuum system, then it was filled with oxygen from the supply cylinder to a pressure of two or three atmospheres and exhausted again. This process removed practically all of the nitrogen originally in the bomb and left it ready for filling to a pressure of about 30 atmospheres for naphthalene combustions or sometimes a higher pressure for sugar and benzoic acid combustions.

After filling to the required pressure, the bomb was removed to the calorimeter, the electrical connections made, and the calorimeter cover and jacket cover put in place, as previously described. The temperature rise was known approximately from the amount of substance to be burned, and the jacket temperature was so adjusted that the final temperature of the calorimeter would be not over a few tenths of a degree, preferably three tenths (see p. 239), above it. Oil was used to retard evaporation from the calorimeter as in the heat capacity observations. The remainder of the observation was carried out as in the case of electric heating except that a second observer was not required. The method of computing the cooling correction, described on page 233, leaves only a single observation to be made during the rapid temperature rise.

4. Form of Observation and Computation Sheet.—Observations were made and computations carried out on specially prepared sheets similar to those used for the heat-capacity observations described above. The following sheet is taken from the records on the combustion of benzoic acid.

TABLE 13
 Department of Commerce
 BUREAU OF STANDARDS
 Washington

COMBUSTION RECORD

			RESISTANCE	TIME	DIF.	SSS.	COILS
T_R	1-52-28						
T_R	1-53-31		27.3308	1-44-42			20.
DT	1-03-63''		9	56	14		5.
r	.0788 corrected		10	45-10	14		2.
rDT	.00050		11	23	14		.2
R	27.33450		12	37			.1.
R_1 corr.	.33500						
	dR	.0037 ω	27.3341	1-51-39	11		
	dT	466''	42	50	13		
	r	.0794	43	52-03	13		
	Mean R	27.333	44	16	12		
	dR	.0004 ω	45	28			
	dT	426''					
	r_2	.094	Fired	52-47			
	Mean R	27.606					
FIRE	1-52-47	Calor.	7602	27.47	53-29		
Substance	B Acid	Bomb	6316 _r				
1913 Sample		Wt.	3500.0				
Wt.	7.9896	Corr.	— .3	27.605	1-55-11		
Cru.	6.5185	Tare	— 409.3	58	48		
Net	1.4711	Vac.	+ 3.4	59	56-15		20.
		Mass	3093.7	59	57-10		5.
O. Pres.	30 Atm.	In place of Standard Mass	58	58-34			2.
Wire	2 cm.	of 3094.0.	57	2-00-42			.5
TR.	4.0 c.c.						.1
Remarks	Correction		3412.4	54	05-40		
	-10.8 Cal.	Excess Mass	— .3				No coil
		Equiv.	3412.1				correc-
T_R	1-58-34						tions are
T_R	1-53-31						signif-
DT	5-03-303''						cant.
r	.0995						
rDT	.00029						
R_2	27.60580						
R_2 corr.	27.60609						
R_1	27.33500						
DR	.27109						
K	10.0690	OUTER BATH					
DT	297296	THERM.					
		Time	Temp.	Room.			
EDT	9313.6	1-43	24905	209 ₃			
Corr.	10.8	2-06	24905	209 ₃			
Cal.	9302.8						
Cal. per gram	6323.8						

5. Corrections.—Aside from the calorimetric corrections already discussed under Section VIII, combustion observations require corrections tabulated on page 242 for heat capacity of the combustible, the oxygen and a small amount of water placed within the bomb to saturate the oxygen, for the heat liberated in the formation of secondary products such as nitric acid, when nitrogen is present in the oxygen, and for the energy supplied in combustion of the ignition or fuse wire used to fire the combustible.

The electric fuse used for igniting the charge in the calorimeter may be either of platinum or iron, but since iron wire burns instead of only melting, it is much more certain to ignite such substances as are easily fused, and for this reason is more commonly used, in spite of the fact that a correction must be applied for the heat supplied by its combustion. The wire generally used weighed 132 mg per meter and the correction for heat liberated in its combustion is 2.25 calories per centimeter, as the heat of formation of iron oxide is about 1600 calories per gram of iron. From 1 to 3 cm were used according to the substance to be ignited. Naphthalene ignited readily with 1 cm while sugar required 3 cm of wire.

A small amount of nitric acid is formed from the nitrogen contained in the oxygen. The amount is nearly proportional to the heat liberated in the combustion and to the percentage of nitrogen present, and was determined by titration after each combustion. The heat of formation of HNO_3 from $\text{N} + \text{O} + \text{H}_2\text{O}$ is about 230 calories per gram of acid. The correction for this nitric acid amounts to 1.45 calories per cubic centimeter of the one-tenth normal NaOH solution used for titration. This correction is applied to the total calories (i. e., heat capacity $\times$ temperature rise).

Apparently in all previous investigations the amount of heat supplied by the electric current during the very short time before the wire melts has been considered negligible. This seemed to be hardly justified and a supplementary experiment was made to determine the magnitude of this quantity. A small copper cylinder was hollowed out and fitted with a copper sleeve in such a way that by running in insulated terminals at the ends, a 1, 2, or 3 cm length of the iron fuse wire could be mounted within this closed copper box and fired in the same way as when mounted in the

calorimeter. In order to guard against partial combustion of the iron by the small amount of oxygen contained in the copper "calorimeter" the openings were made tight with wax, after forcing carbon dioxide through the inclosed space to drive out the air. This copper "calorimeter" was about 12 mm in diameter, 30 mm long, and had a water equivalent of 3 g. In order to measure the rise in temperature of this small mass of copper a fine constantan wire was soldered at one end to it and at the other end to a solid bar of copper of similar dimensions and the circuit was closed through a galvanometer by means of copper leads. This arrangement gave a sensitive calorimetric device which was calibrated by replacing the iron wire by a platinum wire and supplying energy by means of an electric current while measuring the current and voltage by means of a milliammeter and a voltmeter. The calibration gave a deflection of 2.45 cm on the galvanometer scale for 1 joule supplied to the "calorimeter." Experiments with the iron wire melted out by the current from two storage cells in series for each 2 cm of length, and no external resistance, gave for the energy supplied to melt the wire, 0.5 calorie per cm of wire. This correction for a length of 3 cm of wire is not quite negligible.

A number of combustions were made with different amounts of oxygen present in the different bombs, and it was found that when the amount of oxygen was much less than two and one-half times that required to unite with the combustible charge, there were often evidences of incomplete combustion as indicated by a reduction in the total heat liberated as well as by the occasional presence of a slight amount of soot, and by the odor of the products of combustion.

When the amount of oxygen was increased to three times that required to unite with the charge no indications of incomplete combustion were observed, except in rare instances, and no further changes in the observed heat of combustion were noted with further increases in the amount of oxygen employed.

A further check on the completeness of combustion is afforded by the fact that analyses of the products failed to show the presence of carbon monoxide.

X. RESULTS OF COMBUSTION EXPERIMENTS

Observation of the heats of combustion of the three substances sugar, benzoic acid, and naphthalene, as well as of the heat capacity of the bomb, have been carried out intermittently for more than three years by the author, and of late by other observers as well, for study and certification of standard samples of the above materials.

The mass of data collected to date is so great that only a comparatively brief summary of it can be given. The number of combustions amounts to some hundreds. In general, a single observation very seldom departs from the general mean of corresponding observations by much more than 1 part in 1000. Some of the earlier work in the earlier form of calorimeter did not show quite so good agreement.

1. **Naphthalene.**—A series of 17 observations in February, 1910, on five different samples gave 9617 calories per gram weight in air against brass weights with a mean variation of 3.4 calories and a maximum difference from the mean of 11 calories.

A series of 101 observations was made between March and November, 1910, upon four lots obtained from three different dealers, the quality ranging from "highest purity" to "crude flakes." Samples from these various lots were prepared as follows: (1) Unpurified, (2) purified by crystallizing from alcohol, (3) by subliming this sample once, and (4) by recrystallizing from a mixture of liquids having the same heat of combustion as naphthalene. (See Mr. Morey's report.) Tests were made on the original material and on the three prepared samples. The results of this series of observations are tabulated below.

TABLE 14

Heats of Combustion of Various Samples of Naphthalene

	Lot 1. Kahlbaum highest purity	Lot 2. Merck crude flakes	Lot 3. Merck best	Lot 4. Eimer & Amend best imported
Sample 1.....	9618.7—4 obs.	9617.1—4 obs.	9620.6—3 obs.	9615.8—3 obs.
Sample 2.....	9620.1—4 obs.	9618.2—4 obs.		
Sample 3.....	9621.3—4 obs.	9619.4—20 obs.	9615.8—4 obs.	9620.1—12 obs.
Sample 4.....	9623.7—4 obs.	9620.1—5 obs.	9622.0—4 obs.	

This table includes all the observations made with bomb 6316, on the given samples. A few observations with the "Williams" bomb gave results lower by about 3 parts in 10 000. These latter are not given the same weight as those with bomb 6316, since only a small number of observations had been made on the heat capacity of the "Williams" bomb.

While these results indicate in each lot of material a slight increase in the heat of combustion with progressive purification, the maximum difference between any two of the values is less than 1 part in 1000. The mean deviation of the original individual observations from the general mean, taken without regard to the samples, is less than 3.0 calories, i. e., only perhaps 50 per cent more than would be expected from a series of observations with a single sample. This indicates that naphthalene as obtained on the market differs in general by less than 1 part in 1000 in heat of combustion from the purest material.

All the observations up to this point were made in the earlier calorimeter No. 6583.

A series of six observations made in April, 1912, with calorimeter 7602 on a sample of naphthalene prepared for standard samples, gave 9618.8 with a mean deviation of 1.9 and a maximum deviation of 3.5.

A series of 12 observations made in August, 1912, with calorimeter No. 7602, using an entirely new determination of the heat capacity of the calorimeter and a newly prepared sample of naphthalene gave 9623.6 with a mean deviation of 2.1 calories and a maximum deviation of 4.2 calories.

The weighted mean of the foregoing results for the heat of combustion of naphthalene is 9622 ± 2 calories (20°) per gram, weighed in air.

2. Benzoic Acid.—A series of 14 observations made with calorimeter No. 6583 in February, 1910, on four samples purified by several methods from a single lot of material, gave 6328 calories, with a mean deviation of 4.5 and a maximum deviation of 10. The observations on different samples showed no systematic difference, hence all are averaged together. A series of five obser-

vations made in April, 1912, with calorimeter 7602, gave 6331 calories with a mean deviation of 3.0 and a maximum deviation of 5.1.

A series of 11 observations made in September, 1912, on a newly prepared sample, gave 6330 ± 1.8 calories (mean deviation).

A series of nine observations in May, 1913, on a newly prepared sample gave 6329 ± 1.4 calories (mean deviation).

The weighted mean of the foregoing results for the heat of combustion of benzoic acid is 6329 ± 2 calories (20°) per gram, weighed in air.

3. Sucrose or Cane Sugar.—A series of 12 observations made in February, 1910, with calorimeter No. 6583, gave 3951 calories with a mean deviation of 3 and a maximum deviation of 6 calories.

A series of 14 observations made in September, 1912, with calorimeter No. 7602, gave 3948 ± 1.1 calories.

The weighted mean of the foregoing results for the heat of combustion of pure sucrose is 3949 ± 2 calories (20°) per gram, weighed in air.

4. Review.—The following table of comparative results, in so far as the available data will permit, is given in terms of 15° calories instead of 20° calories and for the substances as weighed in air against brass weights. Wrede gives the following figures for specific gravities: Naphthalene 1.145, benzoic acid 1.34, and sucrose 1.58. The results of Fischer and Wrede and of Wrede are expressed in kilo-joules and for weights in vacuo. The former reduced their results to calories by means of the ratio 4.177 for the calorie to the joule, a figure which differs by more than 2 parts in 1000 from that deduced from observations in this investigation (p. 237). The results of both Fischer and Wrede and of Wrede, however, have been reduced to 15° calories by Roth for the Landolt and Börnstein tables, by the use of the ratio 4.189, and as this figure seems much more nearly the correct one, the results quoted below for these authors are those as recomputed by Roth.

TABLE 15

Résumé of Previous Results

Authority	Naptha- lene	Benzoic acid	Sucrose	Date
Stohmann, Rodatz, Hertzberg.....		6315		1887
Berthelot, Vieille.....			3962	1887
Berthelot, Luginin.....		6322		1888
Berthelot, Recoura.....		6345		1888
Stohmann, Kleber, Langbein.....	{ 9628 9619 }	{ 6322		1889
Stohmann, Langbein.....			3955	1892
Atwater and Snell.....			3959	1903
Fischer and Wrede.....	9641			1904
Fries.....		{ 6334 6318		1907 1910
Fischer and Wrede.....		6325	3952	1909
Wrede.....	9633	6323	3952	1910
Roth.....	9643			1910
Leroux.....	9631			1910
Dickinson.....	¹⁸ 9612	¹⁸ 6323	¹⁸ 3945	{ 1910 1912

¹⁸ Here reduced to a basis of 15° calories (by division by 0.999) for comparison with the other results which are expressed in these units.

A comparison of the above results shows very satisfactory agreement with the later observers on the heat of combustion of benzoic acid but a much less satisfactory agreement for the other substances.

As to the results for naphthalene, the early result of Berthelot's investigations (not given in the table) was 9692, a figure manifestly too high, in the light of later observations. Although Wrede's recorded observations were quite concordant, he particularly notes the fact that he does not consider them very reliable, as he found large variations which he attributes to differences in the structure of the substance depending upon its treatment. The experience of the author has been entirely different from this. As has been noted, samples of naphthalene from widely different sources and of widely different degrees of purity have been examined. Nearly all the observations have been made with samples compressed into briquets but some have been made with blocks cut from the fused material. A number of observations were made with a sample which had been

exposed to bright skylight for several months until it showed a decided brown cast on the surface. Briquets were even made up containing as much as possible of the brown surface layer. The amounts of combustible, the pressure of oxygen, and the shape of combustion crucible were changed over the widest practicable range, but no variations were found comparable with the difference between Wrede's results and the present ones.

The results on sucrose also are somewhat lower than those of other observers. The only apparent explanation for this difference is found in the fact that the present observations are corrected for the heat generated in the firing wire before it is ignited. This correction does not seem to have been made by other observers, and while it could hardly be large enough to account entirely for the differences which exist, its real magnitude can not be estimated from the data published. The effect of this correction on the results for sucrose is greater than on those for benzoic acid, on account of the smaller heat of combustion of the former, and it is more important if a greater length of fuse wire is used with the sucrose charges, as is sometimes done because of the lower inflammability of sucrose.

In view of the agreement among different observers, it would seem that benzoic acid is preferable to either naphthalene or sucrose for the accurate standardization of bomb calorimeters.

XI. SUMMARY

A critical examination of such sources of error in calorimetric measurements as occur in the use of the combustion bomb shows that most of these errors can be avoided or reduced to a negligible quantity by care in the design, construction, and use of the calorimeter.

The cooling corrections for a calorimeter designed in accordance with the conclusions reached can be made by a very simple procedure and with an accuracy corresponding to perhaps 1 part in 10 000 of the total amount of heat measured.

A method of electrical calibration was used, which enables the results of combustion observations to be expressed directly in calories almost independently of the electric units, or if the heat capacity of the electric heating element used in the calibration is

known, to be used to check serious errors in either the calorimetric system or the electrical calibrating system.

Observations have been made with two different calorimeters built especially for the purpose and each calibrated by the above method several times independently. Both calibrations and combustions cover a period of more than three years, during which time hundreds of observations have been made with different electrical equipment, and samples of material obtained from different sources and purified at different times and in different ways.

Determinations of the heat of combustion of naphthalene gave 9622 ± 2 calories (20°) per gram weighed in air, with a maximum deviation from the mean of about 5 in 10 000 for groups of observations upon the same samples and about the same maximum deviation of different groups of observations from the mean of all, regardless of the sample.

Determinations of the heat of combustion of benzoic acid gave 6329 ± 1 calorie (20°) per gram weighed in air, with a maximum deviation of about 1 in 1000 for the earlier experiments and 5 in 10 000 for the later ones. Observations taken on samples, some by no means pure, from different sources, show a maximum deviation of 15 in 10 000 and a mean deviation of 7 in 10 000.

Determinations of the heat of combustion of sucrose, fewer in number, gave 3949 ± 2 calories (20°) per gram weighed in air. The later observations show a maximum deviation of a little less than 1 in 1000 and a mean deviation of about 3 in 10 000, though the earlier ones show a maximum deviation of 15 in 10 000.

It appears that, of the three materials included in this investigation, benzoic acid is the most desirable as a combustion standard, as indicated by the agreement between the results of different observers. Naphthalene has been found very reliable and convenient, although it requires care in handling, since a gram briquet will lose more than 1 mg per hour by sublimation. An accuracy of 3 parts in 10 000 is attainable.

Sucrose seems not to be so well adapted for use as a combustion standard as is benzoic acid because of its lower heat of combustion, its frequent failure to ignite, and the lower precision of the results obtained.

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SPECIFIC HEAT OF COPPER IN THE INTERVAL 0° TO 50° C

WITH A NOTE ON VACUUM-JACKETED CALORIMETERS

By D. R. Harper 3d

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I. OBJECT AND SCOPE OF THE INVESTIGATION

Apology is hardly necessary for another paper on the specific heat of copper, notwithstanding the large number of determinations which have already been published. One who has need of employing a figure for this quantity and turns to tables of physical constants for it finds a discordance that is somewhat discouraging. For example, in one of these the few results quoted which cover a common temperature interval show discrepancies of 2 per cent and those which are not in the same interval can not be reduced to a basis of comparison because the temperature coefficients there indicated¹ vary by 60 per cent of the larger or over 100 per cent of the smaller.

There are similar deficiencies in many lines relating to specific heat determinations, but to supply all these will involve an amount of work far outside the possibilities of the Bureau of Standards. However, those constants which enter directly into the primary standardization work of the Bureau must be determined, and in this way the present investigation has come about. Hence, the temperature range of these measurements is quite limited (15° to 50°), although it is obvious that work over a much wider range is needed.

The investigation is a secondary one, related to the fundamental problem of measuring the specific heat of water at various temperatures and the value of the mechanical equivalent of heat; that is, the number of joules in a calorie. A calorimeter employed for this is constructed largely of rolled electrolytic copper, the heat capacity of which forms between 1 and 2 per cent of the heat capacity of the total system as used. Each per cent error in the value used for the specific heat of copper introduces an error of about 1 part in 10 000 in the results obtained with this calorimeter. For reduction of results of the precision now being attained with it redetermination of the specific heat of copper was found to be necessary. Two independent methods were planned, and the apparatus for both was designed and constructed some years ago. Preliminary experiments at that time showed what might be expected, but the actual measurements had to be postponed on

¹ The example is taken from the widely used Landolt-Börnstein *Physikalisch Chemische Tabellen*, edition of 1905, p. 385.

account of more pressing demands on the time of the author. Apparatus for one method has recently been described² and measurements are well under way. The other method³ forms the subject of this paper. It was originally intended that the two be published together, so that comparison of results might be discussed in the communication, but it does not seem advisable to withhold the work now finished, pending completion of that in progress.

Both methods give the specific heat of copper at a certain temperature; that is, the mean value over a small temperature interval. The range of temperatures is from 15° to 50°, this being the range required for the specific heat of water determination mentioned above. Within this range they of course give the temperature coefficient of the specific heat of copper.

This paper is confined to the experimental side of the subject. In the historical sketch only those papers have been reviewed which describe determinations of the specific heat of copper, and in the account of the results of the present determination no discussion has been attempted of their relation to the theories of specific heat. The variation of specific heat with temperature is of the utmost importance in this connection, and there is great temptation to one who is interested in the subject to comment upon the connection between his results and the various formulæ which have been proposed, but this can not be done without a more thorough treatment of the subject than would be proper here.

II. PREVIOUS DETERMINATIONS

1. HISTORICAL SKETCH

The concept of specific heat was formulated in the latter half of the eighteenth century, and the early developments merit a few words, without much regard to whether or not the investigators included copper in their experiments. But the subject soon claimed the attention of many, and the literature of the nineteenth and twentieth centuries is very voluminous. Only the papers containing the results of measurements made on copper are relevant here. Great care has been taken in an endeavor to make

² Harper: *Physical Review* (II), 1, p. 469; 1913.

³ The method is outlined in *Proceedings of Commencement of the University of Pennsylvania*, June 15, 1910.

the list reviewed below complete, but it must be borne in mind that certain classes of papers—e. g., inaugural dissertations and special reports—occasionally escape cataloguers and abstractors and the attention of their contemporaries by cross reference, so that even their existence is unknown to later workers in the same field.

In Table 1 is presented a chronological survey of the subject, and at the close of the chapter is a résumé with an accompanying table and curves which should be ample to meet the requirements of the general reader. The individual reviews presented in the next few pages may be omitted without breaking the continuity of the paper, although they may be seen to have an obvious purpose, both for the needs of the special reader and for reference in clearing up ambiguities in Table 2.

2. REVIEW OF INDIVIDUAL PAPERS

It is hardly possible to assign definite dates to the work of the very early investigators, and not always possible to ascertain what substances they measured. The roll includes Black, Crawford, Deluc, Irvine, Laplace and Lavoisier, and Wilke.

Black, during his lectures as professor of medicine at Glasgow, performed a number of experiments illustrating different capacities for heat for the same mass of different substances. One of his students and devoted followers, Robison,⁴ assigns to these the approximate date 1765-1770, and from his intimate relations with his teacher can not be many years in error. The results of the experiments were not published, and so it is not recorded whether they included copper.

Irvine⁵ took up the work at Glasgow to which Black was obliged to give less and less attention after 1770. He was the first to publish a clear explanation, disentangling the four entities, specific heat, mass, temperature change, and quantity of heat when more than one was varied at a time.

Crawford⁶ published in 1777 the results of some experiments on capacity for heat made during the few years immediately pre-

⁴ Black: *Lectures on the Elements of Chemistry*, edited by John Robison; edition of 1807, Philadelphia; p. 81, note 1 by Robison on p. 330.

⁵ Irvine: *Essays, Chiefly on Chemical Subjects*, London; 1805.

⁶ Crawford: *Experiments and Observations on Animal Heat*; London, 1777 and 1788; Philadelphia, 1787.

TABLE 1

Determinations of the Specific Heat of Copper—Chronological Résumé

Year.	Name	Temperature range investigated			Method
		Low	0° to 100° (slightly lower or higher included)	High	
18th cent.	Black.....		See individual reviews		
	Crawford.....				
	Deluc.....				
	Laplace and Lavoisier.....				
	Irvine.....				
	Wilke.....				
1817	Dulong and Petit.....		0-100.....	0-300.....	Mixt. & cool.
1831	Potter.....		20-100.....		Mixt.
1834	Hermann.....		10-30.....		Cooling
1835	De la Rive and Marcet.....		5-15.....		Cooling
1840	Regnault.....		15-100.....		Mixt.
1843	Regnault.....		5-20.....		Cooling
1856	Bede.....		15-100.....	16-172; 17-247...	Mixt.
1864	Kopp.....		20-50.....		Mixt.
1881	Lorenz.....		-20 to +20; 20-78; 20-131		Mixt.
1884	Tomlinson.....		20-60; 20-100.....		Mixt.
1887	Naccari.....		17-99.....	17-172; 17-253; 17-321	Mixt.
1891	Zakrzewski.....	-100 to 0.....	0-100.....		Ice cal.
1892	Schütz.....	-78 to +15.....	15-100.....		Mixt.
1892	Le Verrier.....			0 to 1000 in stages	Mixt.
1893	Richards and Frazier.....			0 to 1000.....	Mixt.
1893	Veigt.....		21-100.....		Mixt.
1895	Waterman.....		23-100.....		Isoth. cal.
1895	Bartoli and Stracciati.....		15-100.....		Mixt.
1898	Trewbridge.....	-181 to +11.....	23-100.....		Mixt.
1898	Behn.....	-186 to +18; -79 to +18			Mixt.
1900	Behn.....	Above, continued			Mixt.
1900	Jaeger and Dieselschwerdt.....		At 18°; at 100.....		Cooling
1900	Tilden.....		20-100.....		Steam cal.
1902	Gaede.....		0-100 in small steps		Elect. htg.
1903	Schmitz.....	-182 to +20.....	20-100.....		Mixt.
1904	Glaser.....			To 1000.....	Mixt.
1910	Magnus.....		15-100.....	15-238; 15-338...	Twin cal.
1910	Richards and Jackson.....	-190 to +20.....			Mixt.
1910	Schimpff.....	-190 to +17; -79 to +17	17-100.....		Mixt.
1910	Nernst, Korf, Lind'mann.....		2-21.....		Mixt.
1911	Korf.....	-190 to -83..... -77 to 0			Mixt.
1911	Nernst and Lindemann.....	-250 to -185.....			Elect. htg.
1911	Nernst.....	-250 to -185.....			Elect. htg.
1913	Griffiths and Griffiths.....		0-100 in steps.....		Elect. htg.

ceding. These however did not possess his own confidence and were repeated and considerably extended, an edition of 1788 being much more comprehensive than the earlier ones. The subjects of his experiments included foodstuffs, a few of the more common metals, and also their compounds, and some gases inclosed in a bladder. The method employed was that of mixtures. The result of his measurements of the specific heat of copper⁷ was 0.1111.

Deluc gave much attention to the subject of heat and is frequently cited by his contemporaries in connection with measurements of specific heat, but always without definite references. His memoirs published from 1772 to 1810 were widely scattered, and apparently never collected in a single volume. No reports of experiments were found which contained any measurements for copper.

Laplace and Lavoisier⁸ developed the ice calorimeter in 1780 for the purpose of making specific heat measurements and in that year and in 1783 made a great many determinations, the most of which were published in 1793. They record no measurements on copper.

Wilke⁹ is the author of the term "specific heat," the previous usage having been confined to the term "capacity for heat." He made many experiments and prepared reference tables of specific heats. His experiments with copper gave 0.114 as the specific heat.

Dulong and Petit.¹⁰—The first determinations to possess any claim whatever to accuracy were those made by these authors. The copper was heated to the temperature of steam or of boiling mercury, these temperatures being reduced to the gas scale by means of the results of an elaborate comparison of mercury weight thermometers, air and metal expansion thermometers, in a preliminary investigation. The hot metal was plunged into a calorimeter slightly cooler than the room and the temperature rise measured with a mercurial thermometer. The rise was 5° to 6°,

⁷ Figure for the specific heat of copper from p. 288 of the edition of 1788.

⁸ Laplace and Lavoisier: *Memoirs de l'Academie de Science*, 1780, p. 355; *Oeuvres de Lavoisier*, 2, pp. 283, 724; (1862.)

⁹ Wilke: *Transactions of the Swedish Academy*, various years.

¹⁰ Dulong and Petit: *Journal Ecole Polytechnique*, 11, p. 189, 1800; *Annales de Chimie et de Physique* (2), 7, p. 140; 1817.

and the amount of metal employed 1 to 3 kg. The results are given for even hundred-degree intervals and are expressed in terms of specific heat of water equal to unity. (At that time variation with temperature of the specific heat of water was not generally recognized.)

Temperature interval	0° to 100°	0° to 300°
Mean specific heat	0.0949	0.1013

Two years after the publication of the experiments just described a second communication¹¹ was made, describing a series by the method of cooling. The results were deduced from observations of the time taken to cool from 10° to 5° when suspended in an inclosure surrounded by melting ice. Great care seems to have been taken in all details, and sources of possible error received more than a perfunctory consideration. The mean result was

10° to 5° (apparently this range, but not stated clearly)
0.0949

Potter.¹²—The two papers by this author, in conjunction with the criticism of the work by Johnston¹³ form a contribution that can not be said to inspire confidence. By employing the method of mixtures in two ways, hot copper in cold water and cold copper in hot water, he believed that the systematic errors of this method should reverse and the mean be a better approximation to the truth than would a result obtained by the more usual first method alone. The details of making the measurements were evidently very poorly carried out. The first series of experiments gave as mean results

Hot copper (212° F) in cool water (room temperature)	0.0868	} 0.096,
Cool copper (55° F) in hot water (103° F)	0.1014	

having due regard to reversible and possibly irreversible errors.

A second series, including 18 determinations, gave 0.0943 for the hot copper method; the hot water method was not carried out with copper, but a correction to the other results deduced

¹¹ Dulong and Petit; *Annales de Chimie et de Physique* (2), 10, p. 395; 1819.

¹² Potter: *Edinburgh Journal of Science*, New Series, 5, p. 80, 1831; *ibid.*, 6, p. 163; 1832.

¹³ Johnston: *Ibid.*, 6, p. 265; 1832.

from hot water experiments with other metals; the final figure is stated to be 0.096.

Hermann¹⁴ undertook an elaborate investigation for the purpose of ascertaining the fundamental laws of the relations of specific heats of substances, especially compounds. He deemed a re-determination of the values for simple substances to be advisable and employed the method of cooling. The temperature range was 30° C to 10° C. In terms of the mean specific heat of water over this interval as unity, the result for copper was

0.0961 at (20°).

De la Rive and Marcet¹⁵ read a paper to the Geneva society in 1835 giving the results of many determinations of specific heat by the method of cooling. Copper was often the substance experimented upon, but as they originally obtained the heat capacity of their calorimeter by performing similar experiments with copper and assuming a value for its specific heat, 0.095 from the tables of Dulong and Petit, these numerous experiments are but a test of precision, and the final value of 0.095 which they state in their results is not entitled to consideration as an independent determination.

Regnault¹⁶, amongst many hundred determinations of specific heats, includes two series of measurements on copper. The first of these, by the method of mixtures, was performed with extraordinary care because the sample of copper so standardized was to be employed in determining the specific heat of terebenthine (a turpentine oil) for use in a calorimeter where water could not be used, and was therefore a basis of reference for a whole series of measurements. Four experiments with very pure copper, from 98° C to (about) 17°, gave the following results in terms of water as unity (irrespective of temperature, but may be considered to be in terms of the 15° cal within probably one part in 1000):

0.09537; 0.09546; 0.09497; 0.09480; mean 0.09515.

The work of this experimenter upon the effect of hardness on specific heat is important. A specimen of soft copper was used,

¹⁴ Hermann: *Nouveaux Memoires de la Société Impériale des Naturalistes à Moscou*, 8, p. 137; 1834.

¹⁵ De la Rive et Marcet: *Annales de Chimie et de Physique* (s), 75, p. 113, 1840.

¹⁶ Regnault: *Annales de Chimie et de Physique* (s), 78, p. 5; 1840.

then it was hammered cold, and finally was annealed. The results of the specific heat determinations were:

Soft	Hammered	Soft
0.09501 } 9455 } 0.0948	0.0936 } 933 } 0.0934	0.0949 } 948 } 0.0948.

The procedure for the measurements was almost identical, so that the comparative results are worthy of careful consideration. Whatever systematic errors may characterize Regnault's work due to faulty instruments and especially the state of thermometry, his very great care in every detail of experimental work entitles such a comparison to confidence.

The second series of measurements¹⁷ on copper was made in 1843 by the method of cooling in a partial vacuum (1.5 mm of Hg.). The results obtained at that time for a number of metals were extremely discordant and quite irreconcilable with earlier determinations by the method of mixtures. Regnault never had any confidence in this piece of work, nor did he use the results of it, but also he was not able to find a satisfactory explanation of the fault. The mean result for copper was—

$$0.0886 (20^{\circ} \text{ to } 5^{\circ}).$$

Bede¹⁸ employed the method of mixtures. The copper was heated for an hour or more in a tube immersed in an oil bath, the temperature being measured with a mercurial thermometer. The calorimeter thermometer was calibrated for bore and fundamental interval, the scale being arbitrary. The heat capacity of the calorimeter, about 1 per cent of that of its water content, was computed from the weights and specific heats of the parts. The only cooling correction was to start the experiment somewhat below room temperature, ending it a little above. The operations seem to have been arranged with some care and the chief error is most likely in the thermometry. The average results were:

Temperature interval	15° – 100°	16° – 172°	17° – 247°
Mean specific heat	0.09331	0.09483	0.09680

for pure copper. They are expressed in terms of the specific heat of water equal unity at the mean temperature of an experiment,

¹⁷ Regnault; *Annales de Chimie et de Physique*, (3), 9, p. 322; 1843.

¹⁸ Bede; *Academie de Belgique, Memoires Couronnés*, 27; 1896.

which was nearly always within a degree either side of 15° C. Bede considers a linear law of variation to hold for most metals and expresses the results for copper in the form—

$$c_t = 0.0910 + 0.000046t \quad (\text{specific heat at temperature } t).$$

$$c_o = 0.0910 + 0.000023t \quad (\text{mean value, } 0^{\circ} \text{ to } t^{\circ}).$$

Kopp¹⁹ made an enormous number of specific heat measurements, chiefly of compounds, to definitely establish the laws of their relationship. He showed beyond doubt that the conclusion of Neumann and Avogadro and others regarding the computation of the specific heat of a compound from the specific heats of its constituent elements was thoroughly sound (the law is frequently referred to as Kopp's law). For the purposes of his investigation high accuracy was sacrificed to multiplicity of experiments, and he is very explicit in explaining that the apparatus and procedure were not arranged for precision.

The method was that of mixtures. The substances were placed in a glass tube, surrounded by an inert liquid so that temperature equilibrium with the surroundings of the tube might be more quickly attained. The tube was heated for 10 minutes in a mercury bath immersed in a hot oil bath, and then transferred to the calorimeter. The only account taken of a cooling correction was to start an experiment below room temperature and end it above, the liquid in the tube was not stirred, and also there is a very large correction in the results due to the heat capacity of the tube and its liquid; nevertheless some control experiments with water indicate that the results attained were rather good. The results for copper were:

Immersed in naphtha 0.0895	
949	mean 0.0925 (45° to 15°)
926	
930	
Immersed in naphtha 0.0909	
906	mean 0.0911 (53° to 21°)
917	
902	
921	

¹⁹ Kopp: *Annalen der Chemie und Pharmacie*, 8 supplement; 1864-5.

Immersed in water	0.0965	} mean 0.0953 (50° to 21°)
	958	
	953	
	934	
Final mean, 20° to 50°, 0.0930		

The sample was the commercial copper wire obtainable at that time. The unit in which the result is expressed is immaterial, as the final cipher is certainly gratuitous.

Lorenz²⁰ determined the specific heat of copper in the course of his work on the measurement of conductivities. The method of mixtures was employed. A rod was heated in a tube immersed in the vapor of boiling ethyl alcohol (78°) or amylalcohol (131°), or was cooled with an ice salt mixture (-20°) and plunged into a calorimeter at about 20°, so that results were obtained corresponding to mean temperatures of about 0°, 50°, 75°. The means of several experiments were

$$0^{\circ}: 0.08988 \qquad 50^{\circ}: 0.09169 \qquad 75^{\circ}: 0.09319$$

The author states the true specific heat at 0° to be slightly different from the mean value -20° to +20°, and gives the figures

$$0^{\circ}: 0.08970 \qquad 100^{\circ}: 0.09421$$

There are no details concerning the temperature scale, the heat unit or the corrections, other than to say that the usual method was followed.

Tomlinson²¹ in an investigation on the influence of stress and strain on the properties of materials, determined the specific heat of some commercial copper wire after thorough annealing. The wire was coiled up inside a small brass holder, and with a thermometer in the center of the coil was heated in an air bath to 60° or 100°, and then plunged into the calorimeter. A series of blanks with the brass holder alone was also made. No details of calorimetric procedure are given, but only a blanket statement, "Every precaution was taken both with regard to the instruments themselves and the mode of using them to avoid error, and the formulæ given may be received with great confidence." Unfor-

²⁰ Lorenz: *Wiedemanns Annalen*, 18, p. 434; 1881.

²¹ Tomlinson: *Proceedings of the Royal Society of London*, 87, p. 108; 1884.

tunately the results of this work, which have often been quoted, are sadly misleading (temperature coefficient undoubtedly very erroneous, see Fig. 1). These results, expressed in terms of the 0° calorie are:

$$\begin{aligned}\text{Copper of density } 20^\circ/4^\circ &= 8.851; \\ \text{total heat } 0^\circ \text{ to } t^\circ, & 0.09008t + 0.0000324t^2; \\ \text{specific heat at } t^\circ, & 0.09008 + 0.0000648t.\end{aligned}$$

Naccari²² carried out a very elaborate series of specific heat determinations by the method of mixtures. His thermometry and calorimetry were apparently more careful than were those of any of the preceding investigators and there would seem to be good reason to assign considerable weight to the results. Nevertheless the results with copper show a variation with temperature that can not be reconciled with later determinations (see Fig. 1) pointing to a serious error of some kind not easily ascertainable, which may affect all the experiments. A number of observations were taken in each of several temperature intervals, the mean results being:

$$\begin{aligned}\text{Total heat, } 17^\circ \text{ to } 99^\circ &: 7.68; & 17^\circ \text{ to } 171^\circ &: 14.45; \\ & & 17^\circ \text{ to } 253^\circ &: 22.44; & 17^\circ \text{ to } 321^\circ &: 29.08.\end{aligned}$$

The least square smoothed curve (for total heat) is given as

$$H_{17}^t = 0.092455(t - 17) + 10.629 \times 10^{-6}(t - 17)^2$$

and the true specific heat at t° as

$$c_t = 0.092455 + 21.258 \times 10^{-6}(t - 17) \text{ or } 0.09205(1 + 230.8 \times 10^{-6}t)$$

Zakrzewski²³ measured the specific heats of metals in the ranges -100° to 0° and 0° to $+100^\circ$, using a Bunsen ice calorimeter for the purpose. Cooling to -100° was accomplished in a low-temperature thermostat, the refrigeration for which was obtained by the evaporation of a volatile liquid. The results for copper were:

$$\begin{aligned}-100^\circ \text{ to } 0^\circ & & 0.08514 \\ +100^\circ \text{ to } 0^\circ & & 0.09217\end{aligned}$$

²² Naccari: Reale Accademia delle Scienze di Torino, Atti, 28, p. 107; 1887.

²³ Zakrzewski: Krakau Universitäts Anzeiger, 1891, p. 146 (original paper not accessible for review, which is taken from Fortschritte der Physik, 1891).

Schütz²⁴ measured the specific heats of alloys and amalgams and of the constituent metals. He employed the method of mixtures, using a very small brass calorimeter, about 50 cc, and 30 to 40 grams of copper, so that the temperature change was fairly large. The specimens, little pieces of thick wire placed in a test tube, were cooled in solid carbon dioxide or heated in steam. Temperatures were determined by a thermometer in the midst of the pieces. The low temperature thermometer, an alcohol one, was compared with a specially constructed air thermometer at several points, and in its use stem corrections were taken into consideration. Other details of the measurement seem to have received correspondingly careful attention. The results were

Steam to 15° (about): 0.09307; 9278; 9338; mean 0.0931

Solid carbon dioxide (−78°) to 15°: 0.09041; 9014; mean 0.0903

Le Verrier²⁵ seems to have been the first to measure the specific heat of copper at very high temperatures. The method of mixtures was used and no details are given except that the high temperatures were measured by focussing a Le Chatelier pyrometer on the copper at the instant before plunging it into the calorimeter. The number of observations is not stated.

Temperature interval	Total heat	Mean specific heat
0°–360°	0.104†	0.104
320°–380°	Absorbs 2 cal. near 350°	
360°–580°	37.2+0.125 (t–360)	0.125
560°–600°	Absorbs 2 cal. near 580°	
580°–780°	*37.+0.09 (t–580)	0.09
740°–800°	Absorbs 3.5 cal. near 780°	
780°–1000°	92.+0.118 (t–800)	0.118
	Absorbs 117 cal. about 1020°	

* This figure is obviously a misprint, but all the inconsistencies in the column of total heats can not be so construed.

Richards (J. W.) and Frazier²⁶ made a particular study of copper in a series of measurements of specific heats at high tem-

²⁴ Schütz: Wiedemanns Annalen, 46, p. 177; 1892.

²⁵ Le Verrier: Paris Académie des Sciences, Comptes Rendus, 114, p. 997; 1892.

²⁶ Richards and Frazier: Chemical News, 68, p. 84; 1893.

perature and reached the conclusion that none of the above (Le Verrier's) critical points occur and that the specific heat increases regularly with temperature to 900° according to the formula below. Their work was relative only, a value for the specific heat of platinum taken from other measurements forming the basis of reference. Details of the experiments are not recorded, but they state that it would have been impossible for an absorption of so much heat as 0.5 calorie to have occurred at one of the supposed critical points without detection. Their results were

$$c_t = 0.0939 + 0.00003556t \quad 0^{\circ} \text{ to } 1000^{\circ}$$

Latent heat of fusion (mean of six determinations) = 43.3 cal.

Voigt²⁷ used the method of mixtures. There were no departures from common practice which are worthy of note. By the use of blank experiments and other supplementary experiments bearing upon possible errors, he removed many grounds for suspecting the results, yet it is to be noted that the figure for copper is very low. He claims to have attained an accuracy of 0.2 per cent. The results for copper in terms of $18^{\circ}7$ calories, international hydrogen scale of temperature, were:

21° to 100° , 0.0918; 918; 928; 928; mean, 0.0923.

Waterman²⁸ employed an isothermal calorimeter, running ice water into it immediately after dropping in the hot metal specimen, the rate of supply and the total quantity of ice water being such as to absorb the heat as fast as given up by the metal. The details of all the measurements seem to have received considerable care, and the results indicate a precision that merits a moment's attention to the unit in which they are expressed. This is not explicitly stated, but appears to be the mean heat capacity in the interval 0° to 23° (about) of that mass of water which balances 1 gram of brass (?) in air. Some check on accuracy was obtained by the variation in the quantities of metal and ice water over a range of about two to one. The copper (Lake Superior) was 99.98 per cent pure, and drawn. The mean specific heat from 23° to 100° was found to be

0.09475; 9470; 9467; 9474; average, 0.09471.

²⁷ Voigt: *Wiedemanns Annalen* 49, p. 709; 1893.

²⁸ Waterman: *Physical Review*, 4, p. 161; 1896. *Philosophical Magazine* (5), 40, p. 413; 1895.

Bartoli and Stracciati²⁰ used the method of mixtures, with all details in the usual way. The results given for copper, in terms of 15° calories, were:

Cu with 0.12 % Sn and 0.12 % Au, 0.093392, 15° to 100°

Cu with 0.005 % Sn and traces other metals, 0.093045, 15° to 100°

Trowbridge²⁰ used the method of mixtures. The copper was immersed directly in boiling water and upon removing was rapped sharply against the side of the vessel, the drainage being promoted by rounded ends. Auxiliary experiments gave a correction to be applied for the very small residue of water clinging to the specimen. The calorimetric operations, e. g., thermometry, water equivalent determination, cooling correction, do not appear to have been objects of great care. The exact unit in which results are expressed is immaterial since the observations show large deviations. A process exactly similar was carried out, substituting boiling oxygen for the steam. It was observed that all the oxygen was shaken off the specimen and accordingly no correction was necessary. The temperature of the oxygen was taken as -181°.4. The results were:

23° to 100° 0.09262; 9463; 9399; 9394; 9517; mean 0.0940
-181°.4 to +11° 0.0867; 854; 882; 873; 868; mean 0.0868

Behn²¹ did some very careful work at low temperatures by the method of mixtures. The thermometry was carefully executed with properly standardized instruments, both for the low temperature measurements and the calorimetry. The heat exchanges during transfers of specimens were carefully checked in supplementary experiments, and other details of the measurements were given like attention. The results are expressed in 18° calories, international hydrogen scale of temperature, weighings reduced to vacuo.

Drawn copper containing 0.5 per cent Sb and Ag

-186° to +18°, 0.0796; 0.0795; mean 0.0796

-79° to +18°, 0.0887; 0.0879; 0.0884; mean 0.0883

The small number of observations is not so serious a fault in this

²⁰ Bartoli and Stracciati: Reale Istituto Lombardo di scienze e lettere, *Rendiconti* (2), 28, p. 5; 1895; (original paper not accessible, review from *Fortschritte der Physik*, 1895).

²⁰ Trowbridge: *Science*, new series, 8, p. 6; 1898.

²¹ Behn: *Wiedmanns Annalen*, 66, p. 237; 1898.

investigation as might appear at first, since the method was carefully tried by large numbers of experiments with substances other than copper, and high precision was found to have been secured.

After publication of the first paper the experiments were continued ²² and from the results of both sets the conclusion was drawn that for most metals the variation of specific heat with temperature is expressible by the formula $c = A + Bt + Ct^2$. The later series of experiments are not tabulated in detail. The result ²³ for copper was

$$c = 0.0913 + 0.0000676t - 0.00583t^2$$

but the author states that the work with copper was "not satisfactory."

Jaeger and Diesselhorst ²⁴ determined specific heats as a necessary factor in their measurements of thermal conductivities. The method employed was in principle a method of cooling, the specific heat being determined from the heat lost by a given mass of copper and the corresponding temperature change. In the earlier developments of this method the heat loss was determined from emission constants of the surface obtained from a similar experiment with a substance of known specific heat, usually water; in this investigation the emission constants were obtained by measuring the amount of energy supplied electrically which was necessary to maintain the calorimeter in equilibrium at a given temperature above that of its environment. The calorimeter consisted only of a portion of the metal itself in the form of a rod or wire. A measured current of the desired intensity was sent through the specimen until equilibrium was established and then suddenly interrupted and the rate of cooling observed at intervals. The process was also inverted, a current being suddenly switched on to the specimen and the rate of warming observed, together with the other necessary quantities.

The method worked quite well for poor conductors, but for the better conductors the various quantities involved proved to be so proportioned that it was not feasible to arrange magnitudes

²² Behn: *Annalen der Physik* (4), 1, p. 257; 1900.

²³ 0.0583 stands for 0.00000583 and similarly throughout this paper.

²⁴ Jaeger and Diesselhorst: *Wissenschaftliche Abhandlungen der Physikalisches-Technischen Reichsanstalt*, 2, p. 365; 1900.

that would permit of accurate determination of all. The authors discarded entirely the values of specific heat they found for silver and copper and in the conductivity paper employed values found by Naccari. The results with copper, very pure (less than 0.05 per cent impurity, mostly Fe, Zn), were:

at 18°	0.381	joules per gram degree
at 100°	0.386	

Tilden ²⁵ used a Joly steam calorimeter. The heat unit is that of which 536.5 equal the latent heat of steam at normal pressure. All weighings were reduced to vacuo. The results for pure copper were:

"Room temp." to 100°: 0.09248; 9241; 9205; 9234; mean 0.09232

From sample observations reported in full for other metals, it seems that 20° is a fair figure to take as room temperature.

Some interesting data were obtained concerning the effect of impurities on specific heat. Assuming electrical conductivity to be a criterion of purity, the following results were obtained:

Fairly pure wire (low resistivity), 1.69 microhms per cm cube at 17°.7; 0.09274; 9272; mean 0.09273.

Impure wire (high resistivity), 2.75 microhms per cm cube at 17°.7 (analysis for impurities likely to be present showed no Bi, trace Sb, 0.154 per cent As.); 0.09266; 9267; mean 0.09266.

The difference is not significant.

A sample was then contaminated with known amounts of impurity, and the measurements resulted as follows:

Pure Cu fused in H,	0.09265; 9234; mean 0.0925
Same with 0.002 % P,	0.09368; 9336; mean 0.0935
Same with 0.44 % P,	0.09347; 9320; mean 0.0933
Same with 3.49 % P,	0.09870; 9910; mean 0.0989
Pure Cu fused in air (pos-	
sibly some oxide),	0.0936; 938; mean 0.0937
Same with 0.49 % Sn,	0.0936; mean 0.0936
Same with 3.29 % Sn,	0.0927; 924; mean 0.0925
Same with 6.64 % Sn,	0.0905; 905; mean 0.0905

²⁵ Tilden: *Philosophical Transactions of the Royal Society of London*, A194, p. 233; 1900.

Gaede²⁶ made the first point to point determination by a method electrical in all its features. The specimens of metal formed their own calorimeters. These were machined cylindrical, and a deep central core bored out. Into this was thrust a copper core, wound with a properly insulated heater of constantan ribbon and a resistance thermometer of fine copper wire. Thermal contact between the core and the walls of the well was secured by filling the intervening space with mercury, using a thin steel shell when necessary to avoid amalgamation. This calorimeter was suspended in a thermostat and heated through an accurately measured temperature interval of about 15° by an accurately measured quantity of energy supplied electrically. The apparatus and procedure are described in minute detail, and indicate due care in every respect. The statement of results is faulty in omitting to state the basis of the electrical units and the value of the mechanical equivalent used to obtain the final figures which are said to be in terms of 17° calories and are referred to the international hydrogen scale of temperature. The copper was of high degree of purity, density 8.835.

Temperature, 16°.7 32°.7 47°.0 61°.9 76°.4 92°.3
Specific heat, 0.09108 0.09189 0.09244 0.09310 0.09346 0.09403

These results are expressed by a formula which represents them within ± 0.045 per cent (0° to 100°):

$$c = 0.09111 + 0.00005002 (t-17) - 0.001555 (t-17)^2$$

A linear formula is given also, which represents them within ± 0.09 per cent:

$$c = 0.091225 + 0.0000384 (t-17).$$

Schmitz²⁷ used the method of mixtures as ordinarily carried out, and also an inversion of the Black ice calorimeter method. His paper gives evidence of very careful work in every detail. The specimen was cooled in liquid air, the temperature of which was determined by a resistance thermometer calibrated in boiling

²⁶ Gaede: Inaugural Dissertation, Freiburg, 1902. Short paper in *Physikalische Zeitschrift*, 4, p. 105; 1902.

²⁷ Schmitz: Proceedings of the Royal Society of London, 72, p. 177; 1903.

oxygen taken as $-182^{\circ}.5$. The calorimeter thermometer was of the Beckmann type, carefully standardized and properly used. The reductions were made on the basis of specific heat of water being unity at $17^{\circ}.5$ and varying as tabulated in Griffiths Thermal Measurement of Energy, Table VII.

The copper was very pure; source, Johnson-Mathey Co. The mean of 14 experiments in very good agreement was:

Temp. interval,	Mean specific heat,
-190° to $+20^{\circ}$; 0.800 (mercury scale)	$= 0.0798$ (Hyd. scale).

In the next series of experiments the calorimeter was maintained at 0° as closely as could be measured. The cold copper was then introduced, suspended by a thread from a balance arm. After immersion for a sufficient length of time, it was removed from the calorimeter, carefully dried with filter paper at 0° , and weighed to determine the quantity of the ice coating frozen to it. The latent heat of ice was taken as 80.0. In supplementary experiments were investigated the possible sources of error, such as occluded water, the thread, etc. The results obtained were quite consistent, and the mean of the series with copper is:

-190° to 0° (?): 0.0793

To obtain a comparison with the work of other observers he deemed it advisable to determine the specific heat of the same specimen within the temperature interval 0° to 100° . The method of mixtures was employed, with no variations from the usual practice. The mean of a fairly concordant series of 8 measurements was:

20° to 100° 0.0936 Hydrogen scale; probably $17^{\circ}.5$ calories.

Glaser²⁸ employed crude apparatus, violating most of the established principles of calorimetry, and has indicated the extent to which he appreciated the limitations of work of this character by retaining a few superfluous figures. The method was that of mix-

²⁸ Glaser: *Metallurgie*, 1, p. 103; 1904.

tures in a huge calorimeter, capacity 40 liters or more. The high temperatures were measured with a Le Chatelier pyrometer.

	Mean specific heat
.95.51 % Cu, 1 expt, 891°.5 to 22°.5	0.112405
1 expt, 1081° to 24°	0.158455
Pure Cu, 1 expt, 1005° to 29°	0.10884
1 expt, 1086° to 27°.7	0.152810

Therefore (!) the latent heat of fusion of copper is 41.63 cal.

Magnus³⁹ used a twin calorimeter outfit of very large capacity, about 60 liters. The differential thermometer for this was a 100-junction thermocouple. The water equivalent was determined by immersing copper at 100° in the calorimeter, and also by pouring hot water into it. With the former method the value 0.0933 for the mean specific heat of copper between 15° and 100° was taken, based on the work of Bede and of Naccari.

The results of the two methods were in agreement within the limits of experimental error, and so this may be regarded as an independent determination of the specific heat of copper in terms of a mean 15°–100° calorie. The work was continued at higher temperatures, and the mean results for copper were:

Temperature interval	15°–100°	15°–238°	15°–338°
Mean specific heat	0.0933	0.09510	0.09575

Richards (T. W.) and Jackson⁴⁰ measured specific heats between the temperature of liquid air and 20°. The paper contains a critical review of all previous low temperature determinations. These investigators took especial pains with respect to the apparatus and procedure relating to the low-temperature arrangements, but were somewhat less careful respecting the calorimeter. The description of this indicates possibilities of appreciable errors due to evaporation and to the method of supporting the calorimeter in the jacket. The mean result from ten experiments with copper was:

$$-190^{\circ} \text{ to } +20^{\circ}, 0.0789 \text{ (20}^{\circ} \text{ calories, int. hyd. scale.)}$$

³⁹ Magnus: *Annalen der Physik* (4), 81, p. 597; 1910.

⁴⁰ Richards and Jackson: *Zeitschrift für Physikalische Chemie*, 70, p. 414; 1910.

Schimpff⁴¹ employed the method of mixtures, using a very small calorimeter and rather small quantities of the metal specimens. In consequence his experiments were very liable to error. For example, the thermometer, a large Beckmann instrument, was the source of very great uncertainties respecting water equivalent, heat conduction along its stem, and emergent stem correction. The author claims an accuracy of 1 per cent for his results. The copper was 99.91 per cent pure (Fe 0.02 per cent) and was fused before the measurements. The unit is the 17° calorie, international hydrogen scale, and results of the experiments were:

17° to 100°,	0.0926; 924;	mean 0.0925
17° to - 79°,	0.0880; 889; 872;	mean 0.0880
17° to - 190°,	0.0784; 788;	mean 0.0786

These results were expressed by the formula

$$c_t = 0.091996 + 0.0000457090 (t - 17) - 0.006066 (t - 17)^2$$

giving the following values:

Temperature	- 150°	- 100°	- 50°	0°	+ 50°
Specific heat	0.0674	0.0783	0.0862	0.0910	0.0928

Nernst, Koref, and Lindemann⁴² employed for a calorimeter a large hollow cylinder of copper, with a thermoelement embedded in the wall. Heat exchanges with the surroundings were reduced by suspending this cylinder in vacuo. The method of mixtures was used, the heat gained or lost from the specimen being distributed through the calorimeter by metallic conduction, in contradistinction to the more usual stirred calorimeter liquid. Eight experiments with copper are tabulated, the agreement between them being fair. The mean, in terms of a calorie equal to 4.188 joules (international electric units?), is:

$$21^{\circ}.6 \text{ to } 2^{\circ}.4 \quad 0.0915,$$

Koref⁴³ continued the work with the calorimeter described in the preceding paragraph, obtaining some low temperature meas-

⁴¹ Schimpff: *Zeitschrift für Physikalische Chemie*, 71, p. 257; 1910.

⁴² Nernst, Koref, and Lindemann: *Königlich Preussischen Akademie der Wissenschaften zu Berlin, Sitzungsberichte*, 1910, p. 165; p. 247.

⁴³ Koref: *Annalen der Physik* (4), 88, p. 49; 1911.

urements of specific heats by the method of mixtures. The results for copper (commercial, drawn) were:

Temperature interval.	Mean specific heat.
-189°8 to -83°3	0.0720
-189°8 to -82°9	0.0719
-77°0 to 0°	0.0876
-76°2 to 0°	0.0880

Nernst and Lindemann⁴⁴ made a series of point to point determinations at very low temperatures, using a calorimeter developed by Eucken.⁴⁵ A piece of the metal of suitable size was shaped into a hollow cylinder and a loosely fitting core for the same. On the core was wrapped a platinum wire, properly insulated, to serve as a resistance thermometer and also as an electric heater. The core was placed in the cylinder and paraffin poured into the crevices to improve the thermal contact. The whole was suspended in vacuo, and the specific heat over small temperature intervals determined from measurements of energy supplied electrically and of the temperature rise resulting therefrom. The results of the experiments are given in the paper in the form of a series of curves from which the following values for copper have been read:

Temperature, 40°K	60°	80°	100°
Atomic heat, 0.77	1.87	2.96	3.76
Specific heat, 0.0121	0.0294	0.0465	0.0590
(if at. wt. = 63.6)			

Nernst⁴⁶ in a summary paper of the whole specific heat investigation in which he and his associates had been engaged and had published in parts in the *Berliner Berichte*⁴⁷, gives the results of some measurements with copper that do not appear to have been tabulated elsewhere. They were obtained by the method described in the preceding paragraph, the specimen being about 300 g of electrolytic copper. The unit is a calorie equal to 4.188 joules (international electric units?).

⁴⁴ Nernst and Lindemann: *Königlich Preussischen Akademie der Wissenschaften zu Berlin, Sitzungsberichte*, 1910, p. 263; 1911, p. 306, p. 494.

⁴⁵ Eucken: *Physikalische Zeitschrift*, 10, p. 586; 1909.

⁴⁶ Nernst: *Annalen der Physik* (4), 36, p. 395; 1911.

⁴⁷ Loc. cit.; Notes 42, 44.

Temperature,	23°5K	27°7	33°4	87°	87°	88°
Atomic heat,	0.222	0.324	0.538	3.30	3.36	3.38
Specific heat,	0.0035	0.0051	0.00845	0.0518	0.0527	0.0531
(if at. wt. = 63.6)						

Griffiths and Griffiths⁴⁰ used a twin calorimeter, electric heating, point to point method, the specimen measured forming its own calorimeter. Two exactly similar large cylinders of copper were suspended in a jacketing vessel and a measured amount of energy supplied electrically to one, the temperature rise of which relative to the other was measured by sensitive platinum resistance thermometers connected differentially. Every detail of the experiments seems to have received careful attention, and the precision attained was high, the deviations being generally less than one in one thousand. Some variations of method were introduced where possible for the purpose of securing checks on accuracy, which checks were found satisfactory. These experiments for testing the validity of the method were nearly all performed with copper, so that the number of observations secured with this metal was very large, about 35 in the neighborhood of 0° and 3 or 4 each at the other temperatures noted below. The copper, electrolytically deposited, was very pure, 99.95 per cent, the impurities being Pb, Fe, and a trace of SiO₂.

The results are expressed in a calorie equal to 4.184 electric joules and a temperature scale very closely the hydrogen one. The density of the copper was 8.922.

Temperature,	0°	28°42	67°32	97°4
Specific heat,	0.09088	0.09230	0.09387	0.09521
$c = 0.09088 (1 + 0.0005341t - 0.0048t^2)$				

3. RÉSUMÉ

For convenience of reference are collected in Table 2 the final results of the investigations reviewed in this chapter. To make

⁴⁰ Griffiths and Griffiths: *Philosophical Transactions of the Royal Society of London*, A218, p. 119: 1913.

TABLE 2
The Specific Heat of Copper

Year	Name	Temp.	Result	50° c(DRH)	Remarks
1817	Dulong and Petit	0-100	0.0949	0.094 ₆	
	do	0-300	0.1013		
1819	do	5-10	0.0949	0.097	Method of cooling
1831	Potter	(50°)	0.096	0.10	Mean of expts. over diff. temp. ranges
1834	Hermann	20°	0.0961	0.097 ₄	
1840	Regnault	15-100	0.09515	0.094 ₆	Very pure Cu; Hammered Cu 1.5% lower than soft Cu.
1843	do	"Room"	0.0886	0.09	Method of cooling. (Results consid- ered worthless by Regnault)
1856	Bede	15-100	0.09331	0.093 ₆	Pure copper. Results expressed with- in experimental error by the formula $c=0.0910+0.000046t$
	do	16-172	0.09483		
	do	17-247	0.09680		
1864	Kopp	20-50	0.0930	0.094	Commercial copper wire
1881	Lorenz	0°	0.08988		
	do	50°	0.09169	0.091 ₇	
	do	75°	0.09319		
1884	Tamlinson	(50°)	0.09332	0.093	Mean from expts. in diff. temp. ranges, $c=0.09008+0.0000648t$
1887	Naccari	17-99	0.0937	0.093 ₄	
	do	17-171	0.0938		
	do	17-253	0.0951		
	do	17-321	0.0957		
1891	Zakrzewski	-100-0	0.08514		Bunsen ice calorimeter
	do	0-100	0.09217	0.092 ₆	
1892	Schütz	15-100	0.0931	0.092 ₆	Copper wire
	do	-78-15	0.0903		
1892	Le Verrier	0-360	0.104		
	do	360-580	0.125		
	do	580-780	0.09		
	do	780-1000	0.118		
1893	Richards and Frazier ..	0-1000			$c=0.0939+0.0000356t$
1893	Voigt	21-100	0.923	0.91 ₇	
1895	Waterman	23-100	0.09471	0.094 ₆	Very pure Cu, drawn
1895	Bartoli and Stracciati ..	15-100	0.0932	0.092 ₆	Very pure Cu
1898	Trowbridge	23-100	0.0940	0.093 ₆	
	do	-181.4-11	0.0868		
1900	Bahn	-186-18	0.0796		Drawn copper, 0.5% Sb & Ag. Final result of these expts. and others, not separately reported, $c=0.0913+$ $0.0000676t-0.00583t^2$
	do	-79-18	0.0883		

⁴⁰ This column has been prepared by the author from the figures in the column immediately preceding, which are taken directly from the original papers. In copying them, all the figures stated have been retained; in the column containing the results of the computation of the 50° value by the author, only those figures are retained which the precision (or in some cases apparent accuracy) would seem to warrant. The coefficient 0.000044 has been used in reducing results obtained at the various temperatures to the 50° value to permit of comparison; the formula $c=c_0+0.000044t$ being assumed, valid for values of t from 0° to 100°.

TABLE 2—Continued

Year	Name	Temp.	Result	50° (DRH)	Remarks
1900	Jaeger & Diessehorst....	18°	(0.091 ₀)	0.092	Very pure copper. Method (in principle a method of cooling) not suited to accurate measurements for good conductors. Results considered of no value by Jaeger & Diessehorst.
	do.....	100°	(0.092 ₀)	0.090	
1900	Tilden.....	15-100	0.09232	0.0920	Pure Cu. Expts. showing phosphor raises and tin lowers sp. ht. of Cu
1902	Gaede.....	1697	0.09108	0.0925	Very pure copper. Electric heating, point to point method Results combined in formulas, $c = 0.09111 + 0.00005002(t-17) - 0.001555(t-17)^2$ within $\pm 0.045\%$ $c = 0.09122 + 0.0000384(t-17)$ within $\pm 0.09\%$ Units, 17° calorie, hydrogen scale
	do.....	3297	0.09189	0.0926	
	do.....	4790	0.09244	0.0926	
	do.....	6199	0.09310	0.0926	
	do.....	7694	0.09346	0.0923	
	do.....	9293	0.09403	0.0922	
1903	Schmitz.....	-190-20	0.0798		Very pure copper. 17°5 calorie, hydrogen scale
	do.....	-190-0	0.0793		
	do.....	20-100	0.0936	0.0932	
1904	Glaeser.....	30-1005	0.10884		Pure copper. Procedure such that error of 10% quite probable
1910	Magnus.....	15-100	0.0933	0.093 ₀	20° calories, hydrogen scale
	do.....	15-238	0.09510		
	do.....	15-338	0.09575		
1910	Richards and Jackson.....	-190-20	0.0789		Copper 99.91% pure. Results expressed in formula $c = 0.091996 + 0.0000457090(t-17) - 0.006066(t-17)^2$ Calorie equal to 4.188 joules
1910	Schimpff.....	-190-17	0.0786		
1910	do.....	-79-17	0.0880		
1910	do.....	17-100	0.0925	0.092	Commercial drawn copper. Calorie equal to 4.188 joules
1910	Nernst, Keref, Lindemann	2-22	0.09155	0.0932	
1911	Keref.....	-190-83	0.0720		
1911	do.....	-77-0	0.0876		Calorie equal to 4.188 joules
1911	Nernst and Lindemann.....	-233°	0.012 ₁		
1911	do.....	-213°	0.029 ₁		
1911	do.....	-193°	0.046 ₀		(Assuming ice-point = 273° .1K)
1911	do.....	-173°	0.059 ₀		
1911	Nernst.....	-249°6	0.0035		
1911	do.....	-245°4	0.0051		Electrolytic copper. In terms of a calorie equal to 4.188 joules
1911	do.....	-239°7	0.0084		
1911	do.....	-186°1	0.052		
1911	do.....	-185°1	0.053		Very pure electrolytic copper. Electric heating, point to point method Results expressed by formula $c = 0.09088(1 + 0.0005341t - 0.048t^2)$
1913	Griffiths and Griffiths.....	0°	0.09088	0.0931	
	do.....	28°4	0.09230	0.0932	
	do.....	67°3	0.09387	0.0931	
	do.....	97°4	0.09521	0.0931	

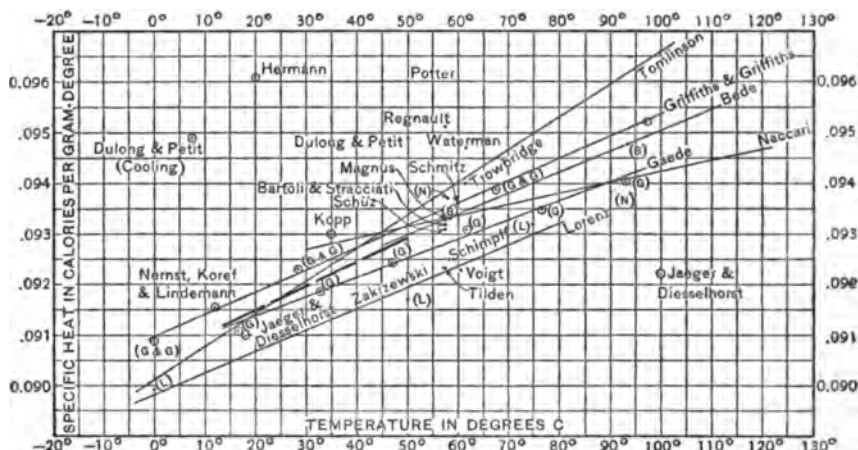
The units in terms of which the above results are expressed are not all the same, but the differences need not be taken into account in making comparisons. In every case the difference between the unit employed and the 15° calorie or the 20° calorie (which differ from each other by about one part in a thousand) is less than the probable experimental error.

comparisons between them reference should be had to Fig. 1. In selecting a figure for the most probable value of the specific heat of copper at a given temperature, it is a most difficult task to ascertain the weight to be assigned to these various measurements. The degree of care shown both in the planning of the experiments and the details of manipulation is reflected to a greater or less extent in each of the papers, and in the foregoing pages an effort has been made to indicate this feature, but it must be borne in mind that the evidence is far from being complete. The older determinations, no matter how skillfully carried out, suffered seriously from lack of adequate facilities and very imperfect knowledge of calorimetry and especially of thermometry. For this reason, it is the opinion of the author that two or three recent investigations executed with due care, that are in agreement, may be relied upon to fix the result with almost no consideration given a host of early determinations. Nevertheless it must be admitted that it is gratifying when one finds that the result so chosen is flanked about equally by the older measurements, and is a source of some anxiety if the departures are all to one side.

The results⁵⁰ obtained by Gaede, by Griffiths and Griffiths, and by the present investigation are in substantial agreement (Fig. 1) respecting the rate of increase with temperature of the specific heat of copper. These investigations were all made with the aid of resistance thermometers for the temperature measurements and precise electrical apparatus for the energy measurements. The details of all three were very carefully considered, and great pains taken to avoid error. Although all three determinations were by methods very similar in principle, the radical differences in working out the details were such as to render infinitesimal the probability of systematic error common to all. The coefficient 0.000044 is accordingly adopted by the author with entire disregard of the other determinations which give a coefficient in the range 0° to 100°, namely Lorenz (1881), 0.000045; Tomlinson (1884), 0.000065; Naccari (1887), 0.000021. The coefficient 0.000044 is then used to reduce to a comparable basis (value at 50°) all of the measurements made in the range 0° to 100°.

To deduce the "most probable value" from these is an operation that can not be devoid of individual opinion (whence the quotation

⁵⁰ Gaede, 0.000040 calories per gram degree at 50°; Griffiths and Griffiths, 0.000044; Harper, 0.000048.



Portion of complete diagram below, greatly magnified (ordinates by a factor of ten; abscissae by factor four)

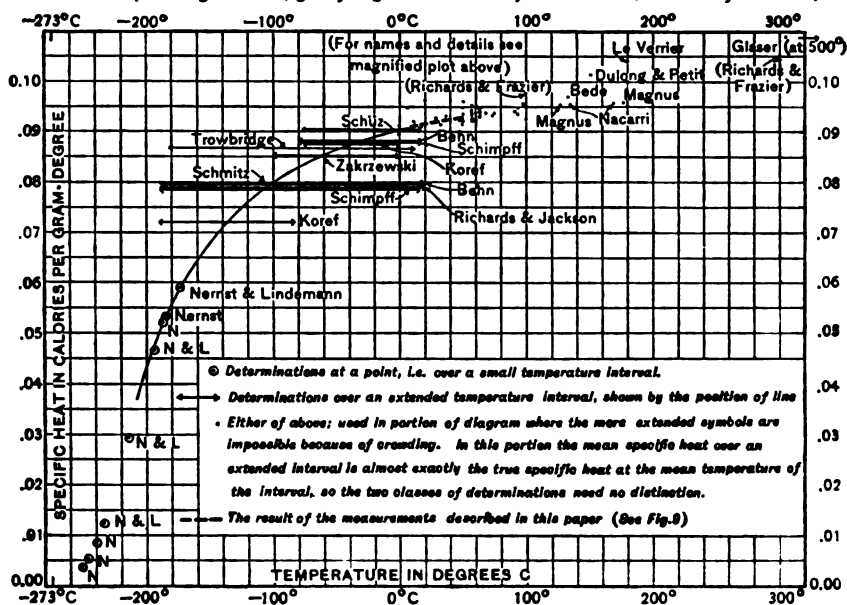


FIG. 1.—The specific heat of copper. Results of measurements made prior to 1914

points). The value selected depends, of course, on the weight assigned to each determination. It is the opinion of the author that 0.0925 is the minimum, 0.0932 the maximum figure to be considered and that in all probability the value lies between 0.0926 and 0.0931, but that closer limits are not defined. If we select the mean of these limits, 0.0928, and the coefficient 0.000044, it is equivalent to collecting the results of all previous measurements of the specific heat of copper between 0° and 100° into the following average figures:

Temperature,	0°	25°	50°	75°	100°
Specific heat,	0.0906	0.0917	0.0928	0.0939	0.0950

Critical analysis of the results obtained outside of the temperature range 0°–100° does not belong to this paper. The low temperature determinations can not be passed by, however, without a comment, often made before, upon the futility of attempting to determine "true specific heat" from mean values over long temperature intervals. As shown in Fig. 1, with the form of the curve well established below the temperature of liquid air by Nernst, and above the temperature of melting ice by Gaede, Griffiths and Griffiths, and the present paper, it is not difficult to supply the intervening portion so as to fit reasonably well the measurements represented by the long lines; but were the entire curve left to determination by such lines, the task would be well nigh hopeless of accurate accomplishment. Above 0°, it has proven correct within reasonable limits to take the mean result of a measurement as the true specific heat at the mean temperature, but this is by no means evident apriori and the assumption might have led into error as serious as it would in the range –200° to 0°. Until the recent point-to-point determinations were made, the common practice of making that assumption had little, if any, justification.

III. METHOD EMPLOYED

The method was simple in principle, although somewhat complex in the details pertaining to the measurements. The important considerations that enter into the determination of each factor are discussed briefly in this section, detailed description both of apparatus and manipulation being reserved for separate sections.

The specimen of copper was a long wire, suspended in vacuo, and connected as part of an electric circuit. A measured quantity of heat could thus be imparted electrically and the temperature rise found by using the specimen itself as a resistance thermometer. The test specimen was thus its own calorimeter, no other substance being included in the "water equivalent" with the single exception of a few grams of mica necessary for electrical insulation.

The chief difficulty encountered was to arrange a large enough amount of copper in a form suitable for the electrical measurements. The wire was compactly coiled into a number of flat spirals, and these, superposed with mica plates between, built up a cylinder (Fig. 3) which included a considerable mass of copper and at the same time possessed electrical resistance large enough to make the necessary electrical measurements with the requisite accuracy. Potential leads tapped in at a distance from the ends of the wire served to define a portion the mass of which was the mass of copper involved in the determination. The resistance of this portion was that which was comprehended in the thermometric factor, and the energy supplied to it was the product of the current in the coil by the potential drop between these leads, integrated over the time the heating circuit was closed.

In equational form, the method may be stated:

$$MSK (R_2 - R_1) = \int_{t_1}^{t_2} e i dt - H. \quad (1)$$

M = mass in grams between potential leads.

S = specific heat (in joules per gram per degree).

K = factor reducing resistance change to temperature change.

R = resistance in ohms (at times t_1 , t_2).

e = drop of potential in volts.

i = current in amperes in specimen between instants t_1 and t_2 .

dt = increment of time in seconds.

H = "heat losses"; taking account of the cooling correction, heat conduction in the lead wires, energy necessarily supplied while measuring R_1 , R_2 , etc.

The surface of unit length of a wire being rather large with respect to the volume, the difficulty of determining H with extreme precision may be readily appreciated, and the feasibility of the method rests largely on the degree of success attained in making H small, so that a reasonable percentage error in its determination

shall be insignificant in the final result. By suspending the wire in vacuo, the cooling correction was reduced to less than half of what it would otherwise have been. The electrical method of heating the specimen in situ by a current traversing it, distributed the heat uniformly, so there was scarcely any lag in the attainment of equilibrium conditions and the measurement of the final temperature could be commenced very shortly after switching off the heating current, thus avoiding any long interval of time in the cooling correction period.

The electrical lead wires conducted an appreciable quantity of heat to or from the specimen and this subject is discussed in the section entitled "Cooling correction." The coil was supported in the vacuum chamber by silk cords, securing excellent thermal and electrical insulation so that any heat loss by conduction along the supports was entirely negligible.

A determination may be outlined as follows:

A small current was switched on to the specimen, heating it very slowly, and was measured by reading the drop of potential across the terminals of a resistance standard in the circuit. These readings alternated with a series taken on the potential leads from the specimen and the slowly rising temperature of the latter, measured by its resistance, was thus defined by a number of readings, constituting the ordinary preperiod of a calorimetric run. With the throw of a switch which exchanged the small current for a large one, the middle period began, and the specimen was heated through the desired range. This was usually 3° to 5° , and the current employed was such as to require seven or eight minutes, giving ample time to secure sufficient potentiometer readings of current and voltage to determine the average power with precision. The time factor of the energy measurement was given by automatic record on a chronograph of the instants when the heavy current was switched on and off. The final temperature of the specimen was determined in exactly the same manner as the initial one.

The precision of measurement of each factor may now be considered. The determination of the energy supplied to the specimen was not a problem offering great difficulty. The ordinary five decade potentiometer reads to one part in fifty thousand on the midsetting, so that moderate care in the selection of a steady storage battery, rheostats of small temperature coefficient and

good contacts, etc., resulted in securing a precision of at least one part in five thousand and probably much better in the measurement of power. The time, say 400 seconds, could be measured to about 0.02 second with the instruments at hand.

The determination of a temperature change of three degrees within one part in five thousand, calls for resistance measurements dependable to one part in five hundred thousand. To this end every feature of precise electrical measurements had to be considered carefully. Properly designed and carefully calibrated auxiliary apparatus was of course essential, and in addition, leakage from unknown sources, thermoelectric disturbances, fluctuations of battery and all similar possibilities of error received care in detection and avoidance. Although for just such reasons as those enumerated, the potentiometer method of reading a resistance thermometer may be as a rule inferior to the Wheatstone bridge method, the author chose the former because of conditions which seemed extremely unfavorable to the bridge method. The leads possessed resistance of the order of that of the coil to be measured, precluding the possibility of precise work with a simple bridge connection. The Thomson double bridge and similar devices eliminating lead resistance require more than one step in adjusting a balance, and appeared unsuited to the measurement of a resistance changing quite so rapidly as in this work.

The mass of the specimen between the potential leads was determined to one part in five thousand or better by direct weighing. The total length of the wire was about 50 meters and the uncertainty of location of the exact junctions of the potential leads was probably within a millimeter each. A slight amount of solder was included in the weighing, but not sufficient to be taken into account.

IV. APPARATUS

1. THE CALORIMETER AND ACCESSORIES

The parts pertaining to the calorimeter are shown in Fig. 2. The specimen (S) forming the calorimeter proper is in the center of the photograph, suspended by silk cords from a circular brass plate which hangs on a clamp stand. This plate is the lid of the vacuum chamber (V) beneath it, and when in use it rested on the

heavy brass reenforcing ring which is just visible at the top of this chamber. The contact surfaces were ground and a lip surrounded the joint so a seal of wax could be poured in if necessary. This was, however, not used, the ground joint proving water-tight. The vacuum around the specimen was secured by exhausting this vessel through the tube (P), the inverted U copper tube (G) at the right being connected to a McLeod gauge.

The outer walls of the evacuated space (i. e., the walls of this chamber) were maintained at uniform temperature by immersion in a well-stirred water bath contained in the large vessel (B) at the right of the figure. An electric heating coil (H), at the extreme left of the figure, was suspended in this water bath and served the double purpose of heating the bath to any desired temperature, and of keeping it there. It would dissipate up to 2 kilowatts safely, heating the bath 2 degrees per minute. When used to maintain a constant temperature it was supplied with current through a relay controlled by a thermostat, shown in the photograph partially hidden by the vacuum chamber. The bulb (T_b) is a long spiral tube of thin glass, and is under the protecting wire screen. The stem (T) with the mercury make and break for the relay circuit can be seen clearly. Immersion in the bath was total except for the mercury in the capillary, and the control of the temperature was all that could be desired.

The relative positions of the parts when assembled may be understood from the picture without description. The course of the circulating water in the large vessel was as follows: Down the offset tube, impelled by the motor-driven propeller stirrer, through a port into the main vessel, passing under the vacuum chamber and striking the thermostat bulb there, rising on all sides of this chamber and flowing back across the top, where it was sucked through an upper port into the offset tube again. The top water surface was several centimeters above the top of the vacuum chamber, so that the tubes inclosing the electrical lead wires (L) from the specimen were immersed for a considerable length, in order that the lead wires might acquire the temperature of the bath as closely as possible no matter how different from room temperature this might be. The thermal contact between these

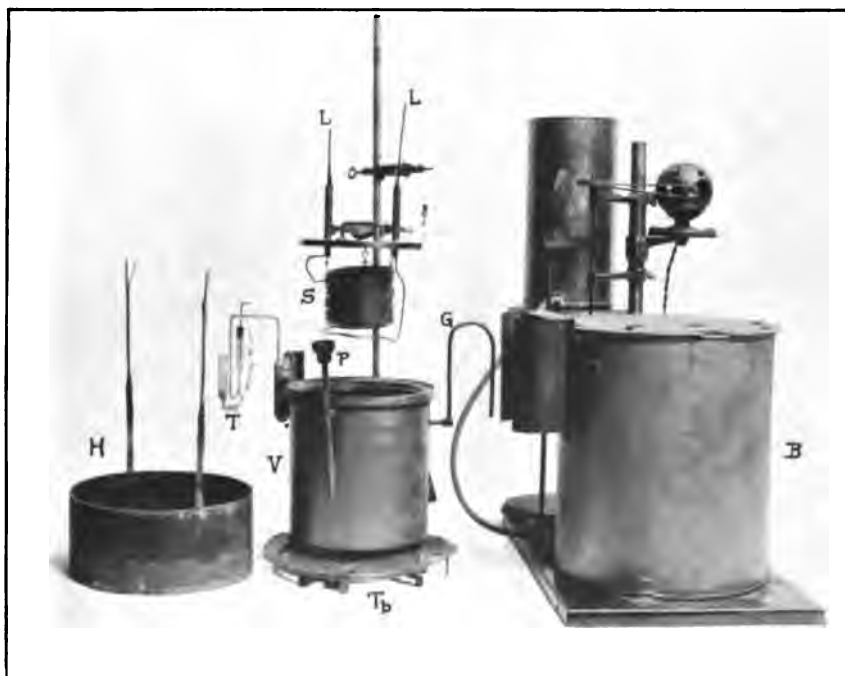


FIG. 2.—The calorimeter. *Detail of parts*

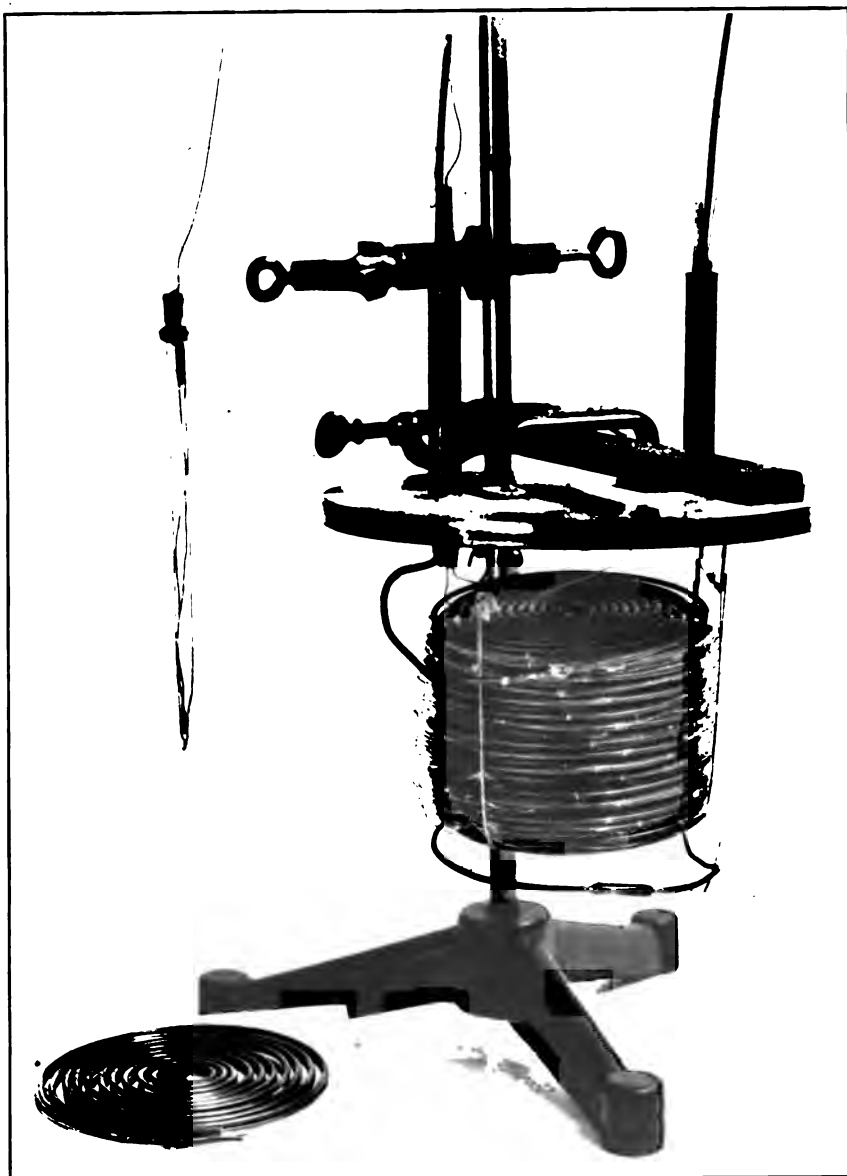


FIG. 3.—Specimen of copper wire in the form used for the specific heat determinations

leads and the bath was fair, considering the necessity of very high electrical insulation and of an absolutely air-tight construction. The leads were bare copper, kept from touching one another by surrounding each by a tube of thin glass, with the space between completely filled with Khotinsky cement, and the glass tubes were embedded in Khotinsky cement in the metal tubes soldered through the brass plate. The construction is shown in both Figures 2 and 3.

Details of the form of the specimen may be seen in Fig. 3. About 50 meters of copper wire 2.5 mm in diameter were coiled into a number of spirals of the form shown in the corner of the figure, each double spiral containing about 3 meters. After winding, the two layers were separated electrically by inserting a very thin plate of mica. Such a unit is noninductive, has a resistance of the order of one one-hundredth of an ohm, and contains about 150 grams of copper. Sixteen of these units were superposed with mica insulation between, forming a cylinder about 10 cm high and 10 cm diameter. Alternate layers were faced in opposite ways and the ends of the wire, previously squared off neatly and tinned, were butt soldered. Uniformity of resistance was thereby easily secured, with no hot spots due to high resistance junctions.

The potential leads were soldered to the centers of the end units, so that the extreme end layers performed no other function than that of current leads, since only the portion of the wire between the potential leads entered into any measurement, as already explained. This design tended to reduce possible error due to thermal conduction along the leads, rather large and therefore requiring precautions in this respect. Over 150 cm of wire separated the specimen from external heat sources or sinks, making the temperature gradient small.

The leads attached to the specimen were five in number, two current leads of copper, approximately 2.5 mm in diameter, two potential leads of enamel-covered copper about 0.3 mm diameter, and one very fine constantan wire, soldered to the copper specimen at a convenient point, making a thermojunction which would indicate the temperature of the specimen relative to the temperature of the other junction of the couple. The latter was

usually dipped in mercury in a thin-walled glass tube immersed in the water bath surrounding the calorimeter, the temperature of this bath being measured with a mercurial thermometer.

The mica insulation forming part of the heat capacity of the calorimeter included 18.5 grams in all, the amount being determined by weighing the mica stock from which the 31 insulating plates were made, and weighing all clippings.

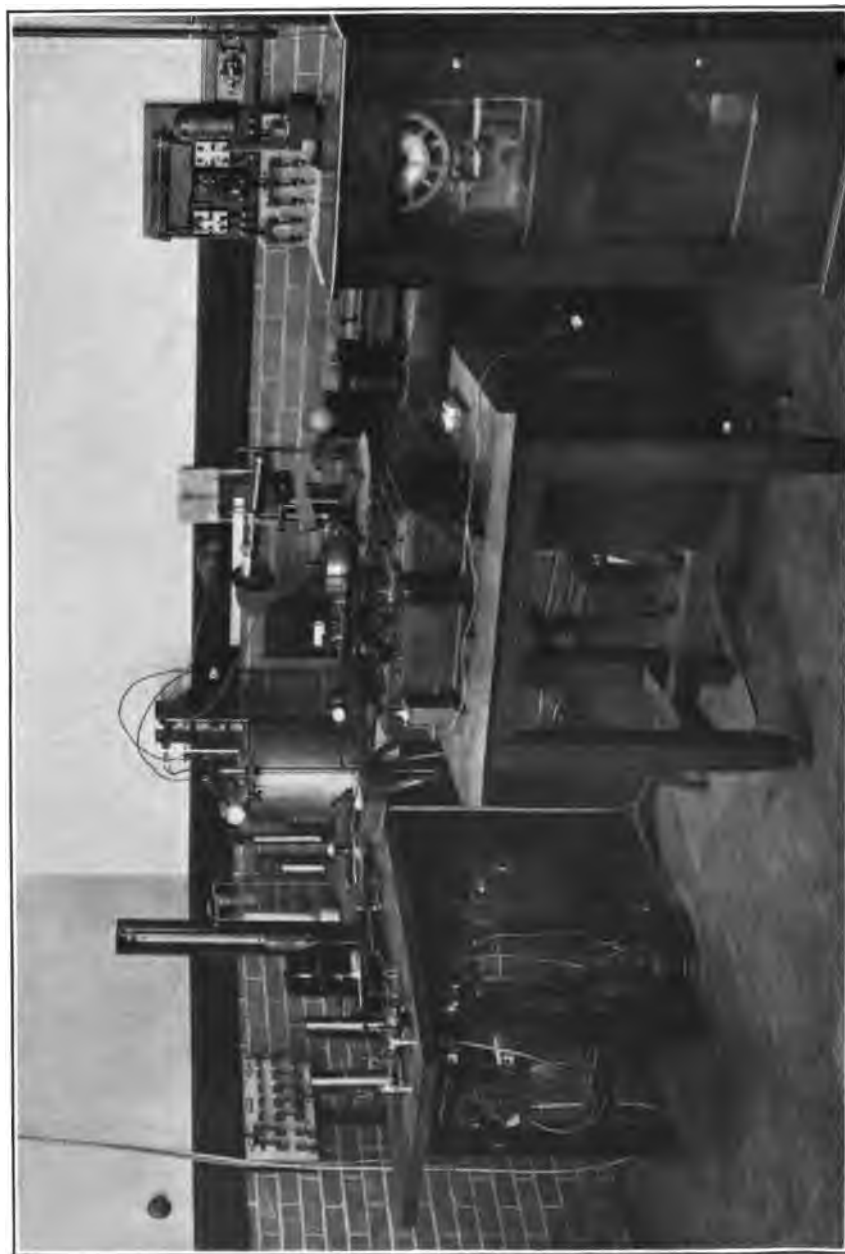
2. ELECTRICAL APPARATUS

A large amount of electrical apparatus was required, a general view of all being shown in Fig. 4. A schematic diagram of the principal circuits forms Fig. 5, in which for the sake of simplicity all detail of the two potentiometer circuits is omitted, also the chronograph circuit and those for the control of the water-bath temperature.

The potentiometer used for the resistance measurements pertaining to the determination of the temperature of the specimen was of the Diesselhorst⁵¹ type constructed by Otto Wolff. This is a low resistance instrument with five dial decades, and as special features avoids errors due to thermal emf generated in the dial contacts and possesses constant galvanometer sensibility, permitting accurate interpolation for a sixth figure. The galvanometer was a Leeds and Northrup instrument of fairly high sensibility and the resistance of the circuit was adjusted so that one microvolt produced a scale deflection of 2 mm. One-tenth microvolt could thus be read without difficulty. In Fig. 4 this potentiometer and accessories are shown in the foreground, on the table at the right of the observer's chair. The galvanometer is just behind the chronograph cabinet.

To the left of the observer's chair, on the wall bench, is the potentiometer system employed for the power measurements. This was a Leeds and Northrup type K slide-wire potentiometer and the galvanometer was a type P instrument of the same maker. This was mounted on the brick wall. Near this potentiometer, between it and the watch, the operating switch (S) of Fig. 5 may be dimly seen, and close at hand were the switches for the control of the chronograph.

⁵¹ *Zeitschrift für Instrumentenkunde*, 26, pp. 173 and 197, 1906; and 28, pp. 1 and 38, 1908.



Gauges
Vacuum Pump

Calorimeter
L. & N. Potentiometer
Dieselhorst Potentiometer

Miscellaneous Electrical Apparatus
Chronograph

FIG. 4.—General view of entire apparatus

The chronograph was of the ticker tape form made by R. Fuess, the tape feeding from the reel at a uniform rate, approximately one cm per second. Seconds were marked by a needle operated from a Riefler clock, the secondary time standard of the Bureau. The reliability of the measurements was about 0.02 second. This chronograph was mounted in a cabinet as a portable unit and appears at the extreme right of Fig. 4.

The resistance standards, rheostats, ammeters, etc., were on the wall bench, mostly hidden in Fig. 4 by the chronograph cabinet. The rheostat (*L*) of Fig. 5 was a bank of carbon lamps and (*r*), (*C*) were Gebr. Ruhstrat rheostats of suitable ranges. All the con-

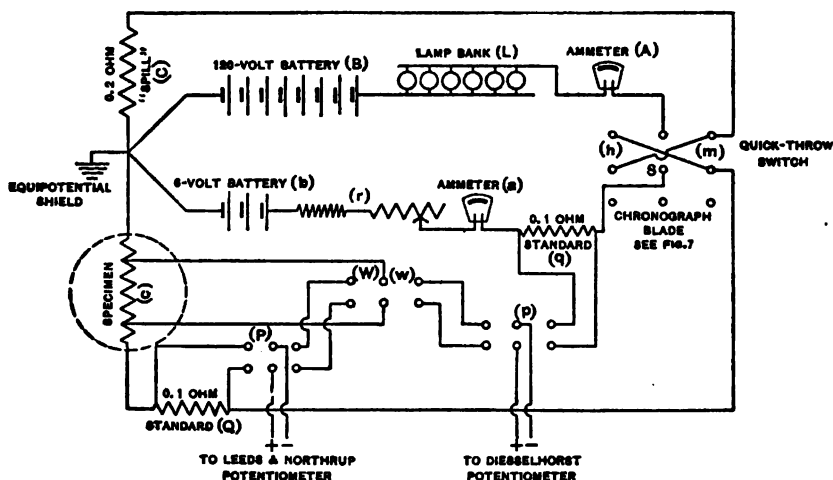


FIG. 5—Diagram of electric circuits

tacts were very good, and in spite of the very exacting requirements, they proved quite satisfactory. The 0.1 ohm resistance standards (*Q*), (*q*), were of manganin of very small temperature coefficient, and were immersed in oil. During the time of an experiment (*q*) was probably constant to better than one part in a million. The absolute value of (*Q*) enters into the measurements, and was determined to within 1 part in 50 000 by comparison with the resistance standards of the Bureau. The standard cell used to adjust the potentiometer current (for the power measurement) was evaluated in terms of the emf standard, and the coils of both potentiometers were carefully calibrated.

3. THE VACUUM PUMP AND ACCESSORIES

The vessel surrounding the calorimeter was exhausted with a May-Nelson rotary pump, a vacuum of the order of 0.2 mm of mercury being the average. The performance of the pump was most unsatisfactory, but no other was available at the time, and the results secured were sufficient for the purpose, as is more fully discussed in the appendix. The residual pressures were measured with a small McLeod gauge, amply sensitive for the purpose. The assembled vacuum apparatus is shown in Fig. 4, mounted as a portable unit on a table at the left. The pump, with its motor and control, and the radiator can for its water-cooling system, were all mounted beneath the table; the McLeod gauge, mercury manometers, stopcocks, etc., being on top.

V. MANIPULATION AND MEASUREMENTS

1. TEMPERATURE CHANGES

(a) CALIBRATION OF THERMOMETER

The exact calibration of the thermometer was postponed to the end of the investigation because the method used necessitated changes in the form of the specimen which would have prevented further heat capacity determinations. An approximate calibration, which need not be described, was made earlier and gave the data necessary for operation of the calorimeter while making those determinations.

Final calibration was accomplished by comparison with two standard platinum resistance thermometers, at 10°, 20°, 30°, 40°, and 50°, in a stirred bath of an oil of good electrical insulating properties. Uniformity of temperature throughout the comparator being essential to the success of this method, it was deemed necessary to remove the mica plates which separated the layers of the copper specimen, so that the oil might be circulated freely, with no pockets of unstirred liquid at uncertain temperature. To prevent contact of adjacent layers of the copper spiral after removing the mica, these were pried a safe distance apart and hard-rubber wedges inserted at appropriate points. When ready for the comparator, the specimen was altered from the appearance shown in Fig. 3 by being elongated to about three times the height shown there.

The comparator was a tall cylindrical vessel of about 10 liters capacity provided with a propeller stirrer in an offset tube and with an electric heating coil. It was protected from drafts and other causes tending to change the rate of cooling, and temperature regulation was obtained by changing the current in the heater. When a very slow, uniform rate of rise or fall of temperature was secured, readings of the standard thermometers and the copper one were taken alternately every 20 or 30 seconds until 10 readings were obtained, 6 of the standards and 4 of the unknown. The sequence of readings was based upon the principle 1, 2, 3, 3, 2, 1, so that the means pertaining to each thermometer were cotemporary and therefore a basis for comparison, provided only that the change of temperature of the bath had not deviated sensibly from a linear relation to the time intervals of reading. In this respect the comparisons at 10° were not satisfactory, as the work was done in a room at 25° and the temperature of the comparator rose so rapidly that it was impossible to time the readings with anything like the necessary precision to have 0.001 significance. For the sake of completeness the measurements made at 10° are tabulated with the rest, but little weight was assigned to them in drawing conclusions.

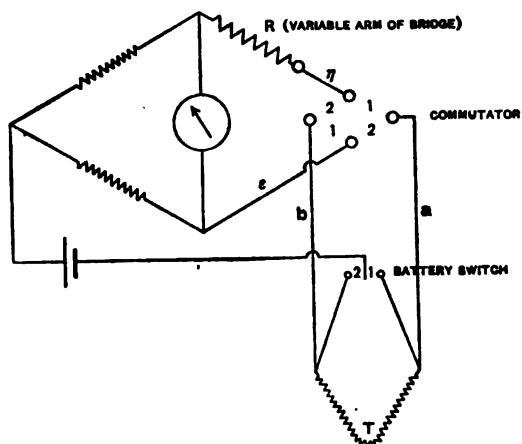
The standard thermometers employed were of the calorimetric type developed by Messrs. Dickinson and Mueller, of this Bureau, and described elsewhere.²⁴ Using them, a temperature difference of 10° could be determined with an accuracy of about one part in ten thousand. The agreement between their simultaneous indications in the comparator bath was quite satisfactory, within a few thousandths of a degree, indicating that no serious lack of uniformity of temperature of the bath existed.

The method of measuring the resistances of the thermometers and the apparatus employed both merit more full description than can be incorporated in this paper. Neither has been described as yet, but it is hoped that both will be the subject of communications from the Bureau in the near future. The Wheatstone bridge was sufficiently sensitive and accurate to have measured the resistances of the standard thermometers to 0.00002 ohm corresponding to 0.0002, but because of the limitations imposed by other considerations it was useless to record more precisely

²⁴ Dickinson and Mueller; *This Bulletin*, 9, p. 483; 1913.

than to the nearest 0.001. The same bridge, with its sensibility increased by increasing the strength of the measuring current, was used to measure the resistance of the copper thermometer to 0.000 002 ohm, corresponding to 0.002. The reliability of these measurements was attested by the results obtained, as will be more fully explained below. The quantity measured was the "branch point resistance" of the copper thermometer plus certain connecting resistances of the Wheatstone bridge. These were constant throughout any one day, and do not affect the differences 10° to 20° to 30°, etc., since they affect each point to exactly the same extent. Through oversight of the fact that differences in these connectors (η , ϵ , of Fig. 6) would interfere with the comparison of different days' results, no pains were taken to keep them the same from day to day, and in making Table 3 it has therefore been necessary to arbitrarily bring the results into agreement at one point (30°), so that the differences at other points would serve as the measure of the variations which occur.

The method, which is that used by E. F. Mueller, of this Bureau, for precision work with the potential lead or "branch point" type of thermometer, required two readings of the thermometer, with commutation by a mercury cup switch, and is most easily described by the equations and Fig. 6.



Commutator in position 1; battery switch also; variable arm adjusted to balance, R_1 ; (ratio arms assumed to be absolutely equal).

$$R_1 + \eta + a = T_1 + b + \epsilon.$$

Commutator reversed to 2; battery switch on 2; variable arm adjusted to balance, now reading R_2 .

$$R_2 + \eta + b = T_2 + a + \epsilon.$$

Add the two equations,⁵³ and a , b , the lead resistances are eliminated.

$$\frac{T_1 + T_2}{2} = \frac{R_1 + R_2}{2} + \eta - \epsilon.$$

FIG. 6.—Wheatstone bridge connections for double Siemens type resistance thermometer, completely eliminating lead resistance by commutation

⁵³ Mr. Mueller's method also includes the elimination of $\eta - \epsilon$ by substituting a short circuiting link for T , and reading the "zero balance" of the bridge $0 = \frac{Z_1 + Z_2}{2} + \eta - \epsilon$; or $\eta - \epsilon = -\frac{Z_1 + Z_2}{2}$

The value of T being desired at a given minute, the balance R_1 was obtained about 10 seconds before this, and R_2 about 10 seconds after the minute. The assumptions made are accordingly (1) that the change of T with time was a linear one; (2) that the total change in the resistance $a-b$ during 20 seconds was negligible in comparison with R .

The effect of η , ϵ , the connecting resistances between the Wheatstone bridge and the commutator, has been sufficiently discussed in an earlier paragraph (p. 296).

Two series of calibration data were obtained by the method just described, and then a crucial test for accuracy was applied by employing a method quite independent, namely, using a potentiometer for the measurement of resistance of the copper coil. The instrument was the Wolff-Diesselhorst potentiometer described in an earlier section (p. 292), and more complete details concerning the method will be found in the next section (p. 300). The method consisted in measuring the ratio of the drop of potential across the terminals of the copper coil to the drop across the terminals of a 0.1 ohm manganin resistance standard when the two were connected in series. The temperature coefficient of the manganin standard was small, about four parts in a million per degree temperature change, so that it was reliable to about one part in a million as a reference standard by which to measure changes in the resistance of the copper. The absolute value of the standard was not accurately known, so that in this case also an arbitrary constant correction is applied to every reading tabulated in Table 3, so as to bring the 30° value to identity with the other 30° values.

The results of the intercomparisons are collected in Table 3. The data comprised therein are as follows: The unit group consisted of 10 readings, 6 on the standards and 4 on the copper coil, at small equal intervals of time. From three to five such groups constituted a determination at a temperature near 10°; then the comparator was heated to 20° and an equal number of readings secured, and so on at 30°, 40°, and 50°.

TABLE 3

Resistance, in Ohms, of the Copper Coil at the Temperatures Shown

Method	10°000	DH.	20°000	DH.	30°000	DH.	40°000	DH.	50°000
Wheatstone bridge.....			0.221666	8776	0.230442	8770	0.239212		
Do.....	0.21286	880 ₂	.221666	8776	.230442	8773	.239215	8775	0.247990
Potentiometer.....	.21287 ₁	8790	.221662	8780	.230442	8771	.239213	8777	.247990
Mean.....			.221665	8777	.230442	8771	.239213	8777	.247990

There is no very good reason for assuming that the resistance of copper after increasing with temperature at a certain rate between 20° and 30° continues at diminished rate between 30° and 40° only to resume the larger value again between 40° and 50°; and there is reason to admit probability of an error as great as 0.0002 in the mean results at any one temperature. The result of the measurement is accordingly taken to be the linear relation

$$R = 0.204119 + 0.008774 t \quad (2)$$

valid between 15° and 50°. The deviations between the formula and the observed results of Table 3 form Table 4. The work done at 10° is almost wholly disregarded for reasons stated above (p. 295).

TABLE 4

Deviations of the Linear Formula (2) from Values of Table 3

	20° 0.221667 ohm	30° 0.230441	40° 0.239215	50° 0.247989
Wheatstone Bridge I.....	+0.000001	- 1	+ 3	
Do. II.....	+ 1	- 1	± 0	- 1
Potentiometer.....	+ 5	- 1	+ 2	- 1
Mean.....	+ 2	- 1	+ 2	- 1

The only part of the result which has significance is the increase in resistance per degree, since the R_0 is arbitrary to the extent of perhaps 0.000020 ohm as already fully explained. Throughout the paper this increase is taken to be 0.008774 ohms per degree; reciprocal 1139.7 equal 1 ohm. This is a temperature coefficient of increase of resistance equal to 0.004298 at 0°, or 0.003958 at 20°, and indicates a very pure grade of copper.⁴⁴

⁴⁴ Dellinger: The Temperature Coefficient of Resistance of Copper, this Bulletin, 7, p. 83, p. 85; 1911.

Temperature Scale.—The unit of temperature in which these measurements are expressed is very closely the degree of the International Hydrogen Scale, as closely so as the reproducibility of this scale admits. The scale actually employed is somewhat more accurately reproducible than is the International Hydrogen Scale and is defined by the following relations:

The "platinum scale" (pt), of the standards employed, by definition,

$$pt = \frac{R_t - R_o}{R_{100} - R_o} 100$$

was very closely the scale which is related to the thermodynamic scale (T) by the value $\delta = 1.49$, substituted in the equation

$$T - pt = \delta \left(\frac{T}{100} - 1 \right) \frac{T}{100}$$

as applied to the observed values of R obtained in ice, steam and sulphur vapor (S. B. P. = 444.95 thermodynamic). It was therefore the scale defined by the purest platinum of Heraeus or of Johnson and Mathey, and is accurately reproducible by using platinum for which the thermometric constants δ and α have the values 1.49 and 0.391 to 0.392 , respectively.

The scale employed (t) was that related to the "platinum scale" of the standards by the equation

$$t - pt = 1.48 \left(\frac{t}{100} - 1 \right) \frac{t}{100}$$

and is therefore as reproducible as the (pt) scale discussed above. The reason for choosing 1.48 rather than 1.50 or any other number which might be arbitrarily selected, is that when the scale so defined by 1.48 was compared⁵⁵ within the interval 0° to 100° to the International Hydrogen Scale, through the medium of the primary mercurial standards by which this scale is distributed⁵⁶ from the Bureau International des Poids et Mesures no differences could be detected which were greater than the uncertainties of the mercurial thermometers.

⁵⁵ The method followed in the comparison was that described in this Bulletin, 8, p. 650; 1907.

⁵⁶ A complete discussion of this subject is given in this Bulletin, 8, p. 663; 1907.

(b) CALORIMETRIC THERMOMETRY

In each experiment for the determination of specific heat, the specimen was heated through a temperature range of the order of 5 degrees, about 0.0044 ohms. That this interval might be measured to an accuracy of about one part in five thousand required that the resistance measurements be made to within 1 microhm. The potentiometer method was employed, the electric circuits being shown in Fig. 5 (p. 293), the switch (S) in position (m).

Current from a three-cell Exide storage battery (b) was regulated to about 0.3 ampere by the rheostat (r). The potential drop across the terminals of the 0.1 ohm standard (q) was therefore about 30 000 microvolts, and across the specimen about 70 000 microvolts. Measurements to 0.1 microvolt therefore corresponded to resistance determinations well within 1 microhm, provided only that the standard remained constant. The power converted to heat by 0.3 ampere in the specimen was about 0.02 watt, which raised the temperature 0°0013 per minute. The heating of the standard can not be readily computed, but as the power was less and the heat capacity many times greater on account of the oil immersion, it is evident that no significant change of temperature occurred within an hour due to the measuring current passing through it. The relation between change of resistance of this manganin standard and change of temperature was about four parts per million for each degree change of temperature (at 25° C).

The resistance of the specimen formed only a small fraction of the total resistance in the circuit, so that a considerable change in its value did not greatly affect the current strength. The drop of potential across the terminals of the 0.1 ohm standard was therefore nearly constant, while that across the specimen was almost directly proportional to the resistance of the latter. The temperature march of the calorimeter was thus given by the "potential" readings on the potentiometer, while the current readings varied only by a very small amount, due to the discharge characteristics of the battery, etc. Accordingly, it seemed desirable to multiply the number of the former at the expense of the latter, and the procedure adopted was as follows:

The potentiometer was read at intervals of 30 seconds, first two potential readings, then with the switch (p) thrown to the other side, one current reading, then two more potential readings, and so on until four pairs of these were obtained with three current readings between, the process consuming five minutes. The potential readings were timed within a second or two; a degree of care which was entirely unnecessary for the nearly constant current readings. Both series of readings were plotted against time and the smooth curves drawn which seemed best to represent the points. While usually linear, these occasionally possessed a slight curvature. The ratio of simultaneous values taken from these curves defined the resistance of the specimen for the instant chosen in terms of the resistance of the standard.

From observations taken in the manner described, data were secured which fixed from a considerable number of individual readings the value to be assigned to the temperature of the specimen at such times as the value was required, both before switching on the heating current and after switching it off. The details of computing the temperature rise of the calorimeter from the data so secured are given in Chapter VI (p. 308).

2. ENERGY SUPPLIED ELECTRICALLY

The determination of the energy supplied to heat the specimen involved the measurement of the average power and the time. The power was measured as the product of potential difference and current, obtaining the latter, however, by a measurement of a potential difference and a resistance of known value.⁶⁷

The circuit is shown diagrammatically in Fig. 5, the switch (S) being in position (h) when the heating current was passing through the specimen. During such interval the measuring current of the circuit (b-r-a-q) was diverted to a "spill" (C) of the same resistance as the specimen, so that the battery (b) was held to constant

⁶⁷ The joule used in this paper is therefore defined by the relation $\frac{e^2}{R}$, where e is in international volts and R is in international ohms. The difference between it and the international joule defined by the relation ei , where i is in international amperes, is certainly less than any amount significant in the results. The international volt is determined by the relation emf of Weston cell at 20° C equals 1.0183 volts; the international ohm is the resistance offered to an unvarying current by a column of pure mercury at 0° C of length 106,300 cm and uniform cross section such that the mass is 14.4527 grams.

discharge rates. Vice versa, during the greater part of the time, when the measuring current traversed the specimen, the heating current traversed the spill so that battery (B) was held constant.

(a) CURRENT STRENGTH

The current strength was maintained nearly constant, the arrangement toward this end being to use a rheostat (L) of resistance many times that of the specimen, and a battery (B) of sufficiently high potential to secure the desired current intensity of about 6 amperes. (B) was about 120 volts, (L) about 20 ohms, and the specimen about 0.2 ohm. A variation of 1 per cent of the resistance of the latter, such as would result from heating it through about 3°, therefore changed the current strength by only one part in 10 000.

The potentiometer was balanced on the drop of potential across the resistance standard (Q) three times during the interval of heating the specimen, once near the beginning, the middle, and the end of the period. The precision of these readings was one part in 60 000 and the time corresponding to a balance was indicated by a signal to a second observer, who read a watch and then recorded the values. Just prior to a series of readings the potentiometer current was adjusted, with the aid of an unsaturated Weston cell, to within 3 parts in 100 000 of its proper value, and at the end of the series this adjustment was checked. The temperature of the resistance standard (Q) was measured with a mercurial thermometer located at the center of the standard and in the oil bath in which the standard was immersed.

(b) POTENTIAL DIFFERENCE

This measurement was accomplished by throwing the switch (P) so as to connect the potential leads from the specimen directly to the potentiometer. Owing to the rapid change of resistance of the specimen while heating, the potential drop across it changed so rapidly as to preclude the possibility of accurate measurement by balancing the slide wire setting at a given moment and reading the value. The inverse method was employed, the instrument being set to a given value, and the corresponding time called off. For example, the potentiometer was set to the value 1.47200, and

when the potential had attained very nearly this value the potentiometer key was held closed for a few seconds, and just as the galvanometer deflection become zero, a signal was given to the other observer; then the potentiometer was set to 1.47300 and the process repeated, and so on. The sensitivity of the galvanometer and precision of setting the slide wire would have permitted obtaining the last figure indicated (fifth decimal place) within two units, but the accuracy of timing was such as to correspond to an error of from three to five such units. It is fairly certain that the figure next the last was obtained correctly (as to precision)—i. e., the measurements were precise to about 1 part in 15 000. Moreover, the errors were accidental rather than systematic,⁸⁸ so that the mean of the series was probably even more reliable. A series was usually composed of 12 readings, 4 groups of 3 each, the three current determinations described in the preceding section (p. 303) being interspersed between the four groups. The increase of the potential difference so measured was found to occur in a strictly linear relation to time, within the limits of accuracy of measurement.

The average power during the interval of heating was accordingly the product of the values of current and potential at the mid-instant, but these values were determined by interpolation from series of 3 and 12 independent settings, respectively, and not from single readings at that instant.

(c) TIME

The time factor of the energy measurements was given by an automatic chronograph record of the instant when switch (S) was closed in position (h) and again when it was returned to position (m). The time actually recorded in the latter instance was not the opening of the heating circuit, but the closing of the other circuit a fraction of a second later. This fraction was

⁸⁸ A systematic error of about 2 parts in 15 000 is introduced by neglecting the lag of the galvanometer. This correction was of the same magnitude and in the same direction for all the experiments, and therefore it was most convenient to neglect it entirely in the computations pertaining to individual experiments and apply only to the final result of the investigation. It is less than one unit in the last figure of this result (p. 315) and is mentioned only to show that the subject received consideration.

The effect of galvanometer lag upon the readings of electrical thermometers is treated in a paper by Harper: this Bulletin, 8, p. 694; 1912.

inappreciable owing to the shape of the switch blade which is shown in Fig. 7.

By reference to Figs. 5 and 7 it may be seen that two blades of (S) carried the calorimeter currents, and that the third was reserved entirely for the chronograph. All three were of the same shape, and bound together by a common handle, so that the contacts were made simultaneously. The operation of the mercury tube shown in Fig. 7 may not be clear without explanation. In the position shown, the only break in the circuit is at (f, y), so that closing this operates the chronograph stylus. Until the circuit is opened at some point, the stylus would remain pressed

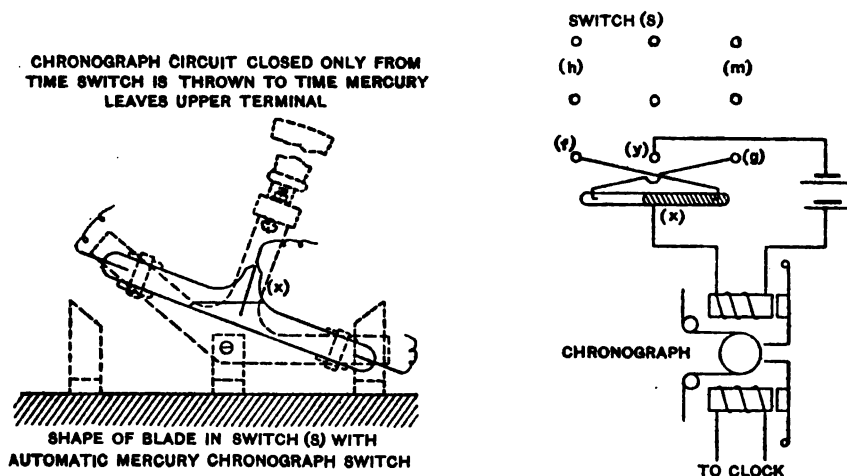


FIG. 7—Details of switch and diagram of chronograph circuits

down against the tape and be useless for further record and also wear unnecessarily. The desired opening of the circuit is effected by the motion of the mercury in the glass tube. Throwing the switch tilts the tube, the mercury flows to the opposite end and the connection (x, f) is broken. The motion of the mercury was damped by glycerine, and the dimensions of the tube and quantity of mercury were such that the break (x, f) and connection of (x, g) occurred after the contact (f, y), never before, the time elapsing being perhaps 0.4 second. It should be noticed that breaking the circuit at (x, f) leaves everything in readiness to record the contact (g, y) when the switch (S) is thrown back to its original position.

3. COOLING CORRECTION

The energy supplied electrically to heat the specimen was not quite all available for this purpose because a certain amount was lost to the surroundings during the progress of the experiment. As actually carried out, this "loss" was usually negative, the calorimeter being cooler than its surroundings during most of the time, but the term "cooling correction" is the customary one and applies equally to cooling or warming. The heat exchange between the specimen and its envelope was computed on the basis of Newton's law of cooling. The cooling constant was determined separately for each individual experiment, inasmuch as its value was a function of the degree of exhaustion of the vacuum chamber, and of the mean temperature of the experiment. The residual pressure varied only slightly during the course of a day's series of experiments, rising a little as if due to a very small leak, and the values found for the cooling constant formed a progression that was very satisfactory.

The data which determined the cooling constant and convergence temperature were used directly in computing the cooling correction, although for the sake of comparison of experiments, the actual value of the constant was usually computed also. These data were the time rates of change of temperature of the calorimeter in the periods just before switching on the heating current and just after switching it off. The rates of change being dependent not only on the exchange of heat between the calorimeter and surroundings, but also on the heat introduced by the small current employed to make the resistance measurements, corrections for the latter were applied in order to secure the basis for the cooling correction computation.

The transfer of heat between the calorimeter and envelope was partly by conduction of the rarefied air, partly by radiation and partly by metallic conduction along the electrical lead wires. Insofar as the latter was proportional to the difference of temperature between the calorimeter and the water bath, it was correctly taken into account by the computations which were based on Newton's law of cooling. This condition would have been realized exactly if the leads in passing through the water bath had acquired its temperature, independent of all outside circumstances. To test

the deviation from such condition the following experiment was carried out.

The water bath was heated to about 50° and maintained at constant temperature by the thermostat system, the room being at about 20° . The calorimeter was heated to the same temperature within a few thousandths of a degree, as measured by the differential thermocouple. The temperature of the calorimeter was then measured every fifteen minutes for an hour or more, and was found to drop regularly to a very slight extent. Had the jacketing been perfect, no such drop would have occurred, since the calorimeter and envelope were at the same temperature and any heat transferred to the room by the lead wires would have been supplied entirely by the water bath and without any effect on the calorimeter. The fall of temperature in an hour was appreciable, but so small that any correction applied for this effect in an interval of seven minutes and with less than 30° temperature difference between calorimeter and room would be less than the limit of accuracy of the measurement of the temperature rise of the specimen, so no correction was applied.

In other words the computations have been carried out on the assumption of heat transfer along the lead wires strictly proportional to the difference of temperature between the calorimeter and its water bath, and therefore additive to the transfers by means of the rarefied gas, and resulting only in giving to the value of the constant in the equations derived from Newton's law a greater magnitude than it would have had if the lead wires had not been present.

4. MASS

The details pertaining to a mass determination are so familiar that they need no description here. The principles involved in securing the proper portion of the wire for the weighing, and the magnitude of the possible errors have both been discussed in Chapter III on "Method," (p. 289). Two weighings were made, one by substitution, using a counterpoise, and the other a double weighing in right and left hand pans successively. The independence of these two methods was a safe check upon the correct reading of the weights. The mass of the specimen was 2254.7 grams.

5. PROGRAM FOR AN EXPERIMENT

The measurement of each quantity having been considered in detail, it remains to sketch briefly how the various steps were interrelated. The main operations prior to a day's series of determinations were the cooling of the specimen to the lowest temperature at which the atmospheric humidity would permit of making the electrical measurements, the exhaustion of the vacuum chamber to a limit set by the pump, and the closing of the circuits to bring the batteries (B, b) (Fig. 5) to a steady discharge condition. A series of from five to nine determinations was then carried out, heating the specimen 3° to 5° in each, stopping when 50° was reached, a limit set at the beginning of the investigation (see p. 260), and in accordance with which the apparatus had been so made that it did not permit of higher temperature without remodeling.

For each experiment the program followed was this: The temperature of the water bath was raised about 3° above that of the calorimeter and the thermostat set to maintain it at this temperature. Then determinations of the temperature of the calorimeter were commenced, following the manner described in the section on measurement of temperature changes (V-1, b, p. 300). These continued during five minutes, and then three or four minutes were devoted to reading the temperature of the room, the temperature of the water bath, the pressure in the vacuum chamber, the temperatures of the resistance standards, and to adjusting the two potentiometer currents to their correct values by the aid of their respective standard cells. A second series of determinations of the temperature of the calorimeter occupied the next five minutes, and in conjunction with the earlier series furnished the data necessary for obtaining both the temperature and its rate of change at the instant of switching on the heating current.

Within the 30 seconds following the close of the readings just described, the switch (W, w) (Fig. 5) was thrown from position (w) to (W), switch (P) was thrown to connect the specimen to the Leeds and Northrup potentiometer which was set to an appropriate value, obtained from the close of the preceding experiment, or by the use of the ammeter (A) and the approximate resistance

of the specimen. Then the chronograph was started, and after the sounder in the circuit beating seconds from the master clock missed a beat, indicating the fifty-ninth second of a minute, the operator threw switch (S) as soon as the next beat occurred. Turning to the potentiometer, the time of balance on the reading previously set was called for an assistant to note, the potentiometer was quickly set to a new value and the power measurement carried out as described in the section on "Energy Supplied Electrically" (V; 2-a, b, p. 302).

Toward the end of the sixth or other chosen minute, the potentiometer readings were discontinued, and following the missing clock beat, the switch (S) was thrown to position (m). (W) was returned to position (w) and readings begun on the Diesselhorst potentiometer to measure the temperature of the specimen and the rate of change thereof. This process consumed two intervals of about five minutes each, with three or four minutes separating the two. Following it, the temperature of the water bath was raised for the succeeding experiment and the entire program repeated.

VI. REDUCTION OF OBSERVATIONS

1. THEORY OF THE COMPUTATION

From the observed data the following working data were computed:

- (1) The values of the following quantities at the instant t_1 when the heating current was switched on:

R_1 , the resistance, in ohms, of the specimen.

r_1 , the rate, in ohms per second, at which this resistance was increasing.

i_1 , the intensity, in amperes, of current used in measuring R_1 .

- (2) The values of similar quantities R_2 , r_2 , i_2 at the instant t_2 when the heating current was switched off.

- (3) The value of W , the quantity of energy supplied electrically between instants t_1 and t_2 . $W = \int_{t_1}^{t_2} e i dt$

The unknown heat capacity, M , may be expressed most conveniently in terms of the joule as a heat unit and the arbitrary resistance scale of temperature, that is in joules per ohm. This can easily be converted later into joules per degree or calories per degree.

The exchange of heat between the calorimeter and its envelope may be expressed with sufficient accuracy⁵⁸ by Newton's law of cooling.

$$-\frac{du}{dt} = \alpha(u - U_e) \quad (3)$$

u = temperature of calorimeter

U_e = temperature of envelope.

Employing the arbitrary resistance scale of this paper,

$$-dR = \alpha(R - R_e)dt \quad (4)$$

gives the change of temperature, while the quantity of heat, if the heat capacity be M , is

$$-MdR = \alpha'(R - R_e)dt$$

designating by α' the quantity of heat gained or lost per second ($dt = 1$) for unit difference of temperature (one ohm) between calorimeter⁵⁹ and envelope.

The energy supplied electrically by current i in an increment of time dt is $eidt$. In the absence of other sources and sinks, that supplied electrically to material of heat capacity M , less that lost to the envelope, raises the temperature of this matter, and the temperature change may be written $r dt$ if r be defined as the rise of temperature per second, $r = \frac{dR}{dt}$. In algebraic terms, then,

$$\left. \begin{aligned} eidt - \alpha'(R - R_e)dt &= Mrdt \\ ei - \alpha'(R - R_e) &= Mr. \end{aligned} \right\} (5)$$

⁵⁸ The total heat interchange, namely the sum of the transfers in both directions, the difference of which transfers forms the actual cooling correction applied, included only about 5 per cent of the total heat involved in an experiment. An error of 5 per cent in its determination would therefore affect the final result by about one part in a thousand.

⁵⁹ The difference between the average temperature of the specimen as measured by its resistance and the surface temperature, which is the one concerned in the radiation losses, etc., is here neglected. For the magnitude of the possible error introduced cf. footnote 59.

This equation expresses the condition at every instant of the experiment. Selecting particular instants, which correspond to the known values,

$$e_1 i_1 - \alpha' (R_1 - R_e) = Mr_1 \quad (6)$$

$$e_2 i_2 - \alpha' (R_2 - R_e) = Mr_2 \quad (7)$$

$$\int_h^h e i dt - \alpha' \int_h^h (R - R_e) dt = M \int_h^i r dt. \quad (8)^{**}$$

The equations (6) and (7) determine the values of α' and R_e for substitution in (8), which then expresses the result of the experiment in terms of the quantities measured.

Since by definition, $r \equiv \frac{dR}{dt}$.

$$\int_h^{i_2} r dt \equiv \int_h^{i_2} \frac{dR}{dt} dt = R_2 - R_1$$

So that (8) may be written in the form

$$W - \alpha' \int_h^h (R - R_e) dt = M(R_2 - R_1) \quad (9)$$

In evaluating the integral, it is to be borne in mind that it is small with respect to the other two terms. Since the heating current was constant to within a few parts in ten thousand, R may be taken as a linear function of time without introducing any error of appreciable magnitude, the heat being supplied in its final distribution without lag.

Substituting a value $R_1 + p(t - t_1)$ for R , where p is defined by $R_2 = R_1 + p(t_2 - t_1)$ and abbreviating $(t_2 - t_1)$ to T , the elimination of α' and R_e results in a reduced form of equation (9) as

$$M = \frac{W - T \left(\frac{R_1 i_1^2 + R_2 i_2^2}{2} \right)}{R_2 - R_1 - T \left(\frac{r_1 + r_2}{2} \right)} \quad (10)$$

From some points of view it is more convenient to express all the small terms as corrections to the observed increase of resistance,

^{**} In equation (8) are neglected second order terms due to the fact that α' and M vary slightly with temperature and therefore with time between instants h and h , and can not be removed from the integrations without such approximation.

20-00	1.5178			18-00	312707	541	0.225941
-38	19			30			
-52	20			19-00	704	551	950
29-08	1.5210 ₆	Mean (2-25-44)	66079	30			
Mean (2-25-44)	1.5076 ₄	Pot. Cor.	00	20-00		577	960
Pot. Cor.	0	Res. Std.	13	30		588	
				21-00	700	614	969
				30			
				22-00		629	
Volts	1.5078	Amperes	0.008 ₄				
Resist. 0.22613 ($R_1=0.22615$)		Power	9.960 ₂				
0.23030 ($R_2=0.23031$)							
on 2-22-14.45	Time 420.11	Energy	4184.1				
off 29-14.56				2-30-00		719350	
				30			
t_2 2-32-00		Calorimeter No.	6907	31-00		336	
				30			
t_1 2-29-14		(Copper spiral)		32-00	312600	292	0.230106
				30			
Δt 166				33-00		276	097
				30			
r_1 0.0 ⁰ 173		Pressure in mm of Hg.	{0.12 at start 0.13 at end}	34-00		245	087
				30		226	
$r_2 \Delta t$ + 28				35-00		597	077
				30		191	
R_2 0.230107		COOLING CONNECTION		36-00		174	067
				30		595	
$R_2 \text{Cor.}$ 0.230136 + 0.00017	$R_1, 1^2=0.0221$	$R_1, 1^2+R_2, 2^2$	$=0.0^222$	37-00		139	
	$R_2, 2^2=0.0225$			30		120	
$R_1 \text{Cor.}$ 0.225881 + 0.00017							
ΔR 0.004184	$r_1=+0.0^0159$	$\frac{r_1+r_2}{2}=+0.0^007$					
	$r_2=-0.0^0173$						
Res. Std. + 3	($T=420$)	+ 0.0^029		2-45-00		718848	
				30	312571		
Cool. Cor. + 12	$420 \times 0.0^029 = +0.000012$			46-00		814	0.229968
				30		800	
ΔR 0.004188				47-00		569	959
				30		764	
K 1139.7	ROOM TEMP.	JACKET		48-00		748	950
				30		565	
$d\theta$ 49751	THERM. 5908	THERM. 6290c		49-00		716	941
				30		699	
Equiv. 880.6	Time	Temp.	Time	Temp.			
Mn. Temp. 0.22823 = 27948	2-05	3093	2-05	27928			
880.6-15.9 (for mica)			2-13	27930			
-864.7 joules/deg. (2254.7g)			2-38	27938			
-0.3835 joules/gram-degree	2-45	30.6	2-50	27942			

FIG. 8.—Laboratory record of an experiment

a practice very common in calorimetric computations. So written

$$M = \frac{W}{(R_2 - R_1) + T \left(\frac{R_1 i_1^2 + R_2 i_2^2}{2M} - \frac{r_1 + r_2}{2} \right)} \quad (11)$$

where a very inexact approximation to the value of M is sufficient to compute the terms $\frac{R i^2}{M}$ with sufficient accuracy.

A comparison of the quantities involved in equation (11) with those enumerated in the opening paragraph of this chapter (p. 308) shows that M is here expressed in terms of quantities all of which are given by the measurements.

2. DETAILS OF COMPUTATION—EXAMPLE

The application of equation (11) to the observed data may be explained with the aid of the sample laboratory record forming Fig. 8. Many of the details have necessarily been described previously and need not be repeated, but are indicated by appropriate references.

W—Energy Supplied Electrically.—The data pertaining to this measurement are collected in the blocks forming the left central portion of the record sheet. Full details regarding the potentiometer readings and the method of determining the mean values have been given. (Chapter V, section 2, p. 301.) To these mean values, 1.5076 and .66079, are applied potentiometer corrections the values of which depend on the setting and on the standard cell used to adjust the potentiometer current. The results are the potential differences across the specimen and the resistance standard. A correction for the departure of this standard resistance from exactly 0.1 ohm is then made and the current in amperes found. The product of the emf and current is labeled "Power," and this multiplied by "Time" is "Energy." The latter²³ is the W of equation (11) and is expressed in joules.

A valuable check is furnished by taking the values of emf and current corresponding to the exact beginning and end of the

²³ Although $E_{AV} \times I_{AV} \times T$ is not mathematically identical with $\int_0^T E i dt$ when both E and i vary (linearly), nevertheless the difference is only of the order of a few parts in ten million when the variation in i is as small as here.

heating period (t_1 , t_2) and using these to compute the resistances for comparison with the resistances R_1 , R_2 found by the more precise measurements. In the example the values found from the "middle period" measurements are 0.22613 at 2-22-14 and 0.23030 at 2-29-14, which are to be compared to 0.22615 and 0.23031 respectively.

T-Time (Duration of the Heating Period).—The chronograph record showed that the current was switched on at 2-22-14.45, (t_1) and off at 2-29-14.56, (t_2), an elapsed time of 420.11 seconds. The mean time of these two, 2-25-44 is that employed for the mean potentiometer readings in the above.

R-Resistance of the Specimen.—Data pertaining to these measurements are tabulated in the long columns to the right of the record sheet. The readings were taken as described in Chapter V, section 1 (b) (p. 300), and after correcting from the calibration certificate of the potentiometer, they were plotted against time as explained in the same section (p. 301) and served to give the resistances at desired even minutes. These appear in the last column, and are expressed in terms of the resistance of the manganin standard (L & N 7354 at 33°.3) and not reduced to international ohms.

In the preperiod the series of values extends to 2-21, so that this value of R , 0.225969, must be employed to determine the value at the desired instant, t_1 , namely 2-22-14, which is 74 seconds later. The computation is given in full in the extreme upper left hand corner of the sheet, and the R_1 *cor* is 0.225981, expressed in units which are reduced to international ohms by adding +0.000170. (The standard resistance was about 0.075 per cent larger than its nominal value, and 0.075 per cent of 0.226 is 0.000170.)

In the afterperiod, inspection of the values corresponding to the times 2-32 to 2-36, leads to a choice of 0.230107 at 2-32-00 rather than 0.230106 given by the single reading at that time. From this the value of R_2 *cor*, corresponding to t_2 , 2-29-14, is obtained, the computations being shown in the lower left corner of Fig. 8. The difference, R_2 *cor* - R_1 *cor*, is 0.004154, expressed in the working unit. The resistance of the 0.1 ohm standard was 0.100075 international ohms, 7.5 parts in 10 000 larger than

the nominal value, which being 3 parts in 4100, gives the correction +3 that is entered just beneath the 0.004154.

r—Rate of Resistance Change.—The computation of the rates r_1 and r_2 is to be found at the top of the sheet (Fig. 8). Between 2-09 and 2-21, the resistance increased 0.000116 ohms and dividing this change by the interval in seconds, gives an average rate r , which is almost exactly the actual rate at the mean time 2-15. At 2-22-14 the rate (r_1) is not greatly different, although slightly so. The correction to obtain it was computed thus: $r = -\alpha (R - R_e)$, so that unless $(R - R_e)$ remain constant, r will vary. R_e , the measure of the temperature of the envelope, may or may not remain constant, but R will certainly change (slightly) by virtue of the cooling or warming of the calorimeter. To find the effect of a change in $(R - R_e)$ on r , differentiate; $dr = -\alpha d(R - R_e)$. In the example, R increased 0.000058 ohms in the six minutes between 2-15 and 2-21, and so if R_e had remained constant, $d(R - R_e)$ would have been +0.000058. The value of α was 0.000080, giving⁸² for $dr = -0.000046$, an appreciable correction to the value of r , 0.00161. However, in this case the temperature of the envelope was rising rapidly, the experiment being carried on at a temperature below that of the room, and when this is taken into account, assuming the change to be nearly linear, the correction evaluates to -0.00002 , instead of -0.00005 as above. The corrected r , 0.00159, may be taken for 2-22 as well as 2-21, and is therefore r_1 . It was used for the determination of $R_{1, cor}$ from the observed value of R obtained 74 seconds before, and also in computing the cooling correction.

Similarly, from the resistances at 2-32 and 2-46, and the corresponding change in the temperature of the envelope, the rate r_2 comes out $(-)0.00173$. This is used to obtain $R_{2, cor}$ from the observed data beginning nearly three minutes later than t_2 , and likewise occurs in the cooling correction. It is for this latter that it is necessary to determine the rates as accurately as here indicated.

Cooling Correction.—This subject has been fully discussed in an earlier section bearing this title (Chapter V, section 3, p. 305). The computation consisted in substituting the proper values in the expression contained in equation (11). All these values occur

⁸² Notation .08 is explained in footnote 33, p. 274.

on the record sheet except M . This was computed approximately and found to be very closely 10^8 , when the unit is joules per ohm (880 joules per degree and 1140 degrees to the ohm). Both i_1 and i_2 were 0.313 amp. The computation is shown in detail in Fig. 8, the result being +0.000012 ohms to be added to the value 0.004157 found for $R_2 - R_1$ (*cor*).

Reduced to degrees by the results of Table 3, the denominator in equation (11) becomes $4^{\circ}.751$, and the result of the experiment is 880.6 joules per degree at a mean temperature of $27^{\circ}.48$. This heat capacity is for 2254.7 grams of copper and 18.5 grams of mica. The specific heat of mica was taken as 0.206 calories per gram·degree,⁴ equal to 0.86 joules per gram·degree, so that the heat capacity of 18.5 grams was taken to be 15.9 joules per degree, and this quantity subtracted from 880.6. The last step in the computation was to divide by the mass of copper and the final figure for this particular experiment was 0.3835 joules per gram·degree at $27^{\circ}.48$.

VII. RESULTS

1. EXPERIMENTS IN 1910

The apparatus was assembled in 1910, when the specimen was built into the form used. Preliminary experiments were made, nine determinations in all, for the purpose of trying the method. While these offered fair evidence that the work was worthy of continuation the results attained were of no other value, and need not be dwelt upon further.

2. EXPERIMENTS IN 1913

In May, June, and July, 1913, 27 determinations were made at various temperatures between 14° and 50° , grouped in five separate series, each of which was begun at the lowest temperature which the prevailing humidity would allow and carried as far as time would permit. The results of these determinations are collected in Table 5 and shown graphically in Fig. 9.

The mean result (Equation 12) is discussed in the next section. Using it to compute the specific heat at the various temperatures listed in the second column, and comparing the results of the

⁴Landolt, Börnstein, Roth: *Physikalisch-Chemische Tabellen*, 1910 edition, p. 759.

computation to those actually observed (fourth column), the differences found are entered under the caption "Deviation."

TABLE 5
Results of Experiments

Date	Mean Temp.	Joules degree	Joules gram-degree	Deviation from equation (12)
1913				
May 30.....	26918	881.5	0.3839	+0.0002
	31.26	883.3	.3847	0
	36.38	887.2	.3864	+ 7
	41.68	888.6	.3871	+ 4
June 4.....	27917	882.2	.3842	+0.0004
	31.93	883.3	.3847	- 1
	37.61	884.7	.3853	- 6
June 10.....	14932	876.3	.3816	+0.0003
	18.29	876.1	.3815	- 6
	22.05	878.2	.3824	- 4
	25.25	879.5	.3830	- 5
	28.46	881.1	.3837	- 4
	31.69	885.5	.3857	+ 10
	35.00	884.1	.3850	- 4
	38.34	885.4	.3856	- 4
June 27.....	26920	881.8	.3840	+0.0003
	29.81	884.1	.3851	+ 7
	33.18	884.4	.3852	+ 2
	36.32	885.5	.3857	0
	39.46	(Accident)	----	-----
	42.72	887.6	.3866	- 3
	46.10	888.7	.3871	- 5
July 28.....	22961	878.5	.3826	-0.0003
	27.48	880.6	.3835	- 4
	32.31	883.5	.3848	- 1
	37.28	886.5	.3861	+ 2
	42.38	887.8	.3867	- 1
	46.77	890.8	.3880	+ 3

Mean result, $0.3834 + 0.00020 (t - 25)$

(12)

Average deviation of observed values from this mean, 0.00036, or very closely one part in one thousand.

3. THE SPECIFIC HEAT AT 25° AND THE TEMPERATURE COEFFICIENT

It is evident from Fig. 9 that within the limited interval of 15° to 50° the relation of the specific heat of copper to temperature may be represented by a straight line as well as, if not better than, by any other curve. Employing the relation $c = c_{25} + \beta (t - 25)$ and assigning equal weight to all the observations in Table 5, a least square solution gives $c_{25} = 0.3834$ and $\beta = 0.00020$.

Chemical analysis by J. A. Scherrer of the Bureau, using a representative sample of the wire, showed a purity of 99.87 per cent. High degree of purity was also indicated by the electrical

properties, the temperature coefficient of increase of resistance, 0.00396 at 20°, indicating 100.5 per cent conductivity of "pure" copper by the old much-used "Matthiesen standard."

The density was 8.86. The wire having been once annealed in the process of manufacture, was of course hardened slightly in the process of shaping into spirals and was not again annealed.

VIII. SUMMARY

1. A critical review of all previous determinations of the specific heat of copper is given in extenso. For the general reader the essentials of this are condensed into two tables and a short explanatory note. The determinations in the temperature range 0–100° are interpreted to indicate that the specific heat of copper (hard-drawn probably excepted) at 50° is between 0.0926 and 0.0931.

2. The general principles of the method employed in this determination are discussed, together with a consideration of the precision necessary in measuring the various quantities, and a full description of the apparatus and the details of making each measurement follow. Fifty meters of copper wire 2.5 mm in diameter served the fourfold function of being at the same time the test specimen, the calorimeter itself, the heater, and the thermometer. Suspended in vacuo and heated with a measured quantity of energy supplied electrically, the resulting temperature rise was measured by the change in resistance.

3. Sources of possible error are carefully considered in the separate discussions pertaining to the measurement of each factor. The precision and the magnitude of the several correction terms are fully indicated by detailed explanation accompanying a sample laboratory record of an experiment.

4. The copper was annealed wire, 99.87 per cent pure, according to chemical analysis, high degree of purity being likewise indicated by the electrical properties.

5. The results of 27 determinations at temperatures between 15° and 50° possess an average deviation of one part in a thousand from

0.383₄ + 0.00020(*t* – 25) international joules per gram degree
equivalent to

0.0917 + 0.000048(*t* – 25) calories, per gram degree

if 4.182 joules equal one 20° calorie.

6. Appended to the paper is a discussion of the use of the vacuum jacket as a means of reducing the cooling correction in calorimetry, the relative magnitudes of the heat transfer due to conduction by air in various stages of rarefaction, and to radiation from some of the more commonly used surfaces being compared. The note is intended to indicate the degree of exhaustion profitable to attain for a given set of fixed radiation conditions when thermal insulation by means of a vacuum jacket is planned.

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WASHINGTON, May 30, 1914.

APPENDIX

NOTE ON VACUUM JACKETED CALORIMETERS

With Especial Reference to the Degree of Thermal Insulation Secured by the Use of a Vacuum Jacket

INTRODUCTION

At the beginning of this investigation it was assumed that the improvement in thermal insulation secured by the use of the vacuum jacket would justify the very considerable disadvantages both in design of calorimeter and manipulation which were introduced thereby. That this was somewhat doubtful developed as soon as some of the heat-transfer measurements were made, as may be seen from the following pages.

However, the difficulties attendant upon exhausting the air space were not without compensation by reason of a material increase in the confidence to be placed in the accuracy of the cooling correction of the calorimeter for causes quite apart from reduction of the magnitude of the correction. In ordinary calorimetric procedure the cooling corrections are computed from data which are obtained while the calorimeter temperature is changing very slowly, i. e., "drifting" slowly at very nearly constant rate toward the jacket temperature, and are applied for the period in which the calorimeter temperature is changing very rapidly. It is a bold assumption that the convection currents existing in the quasi equilibrium state effect the same result in transfer of heat as do the convection currents existing in the very disturbed state,⁶ which assumption is justified only if the conclusions to which it leads are substantiated by experimental test. This seems to be the case, at least within fair limits, with an air gap of approximately 1 cm separating calorimeter and jacket, but with the very wide gap of 5 cm or more with which this calorimeter was constructed there is much greater reason for doubt. Since neither radiation nor conduction is subject to the same uncertainty, the entire absence of convection by reason of exhaustion to a small fraction of an atmosphere affords a much greater degree of confidence in the accuracy of the cooling correction.

⁶ Dickinson, Combustion Calorimetry: this Bulletin 11, p. 190, 1914.

GENERAL CONSIDERATIONS

The efficacy of a vacuum jacket in securing thermal insulation merits some discussion in view of a more or less common tendency to overrate it, or at least to carry evacuation far beyond the necessary or useful stage, frequently at the sacrifice of very considerable time and trouble in arranging apparatus to do so. No degree of exhaustion can reduce heat transfers below the limit set by radiation, and furthermore, when conduction and convection have been reduced to less than the radiation it is obvious that the advantage of continued pumping diminishes rapidly.

The magnitude of the radiation in any given case is therefore the first quantity to claim consideration. Since this paper is concerned only with the heat transfer due to small differences of temperature at ordinary room temperatures, the calculations may be limited to such conditions. From the Stefan Boltzman law

$$\frac{dQ}{dt} = \sigma(T_1^4 - T_2^4)$$

$\frac{dQ}{dt}$ = quantity of heat radiated per second.

T_1 = absolute temperature of radiator.

T_2 = absolute temperature of absorber.

the quantity of heat lost per second by unit area of a black surface at 301° K completely inclosed in a black chamber at 300° K (27° C, the temperature of a warm room) is

$$\begin{aligned}\frac{dQ}{dt} &= 5.7 \times 10^{-12} (301^4 - 300^4) \\ &= 0.00063 \text{ watts (per cm}^2 \text{ per degree C)}\end{aligned}$$

This quantity is compared in Table 6 to others which have a bearing upon the subject. This table does not contain data pertaining to wires and very small pipes, which subject is further discussed below, but contains all the data pertaining to conditions resembling those occurring in calorimetry, which the author could assemble from the literature. Excluding MacFarlane's results, the convection-conduction ranges from about 0.00020 to 0.00070 watts (per cm² per degree) with every indication that the smaller of these two figures is about what one may expect to be true for a piece of apparatus built so as to confine the air circulation in about the same manner as does a calorimeter, which jacketing arrangement is rather common for both scientific and industrial apparatus. Since 0.00020 watts per cm² per degree is about 30 per cent of the figure computed above for black radiation, another

way of stating this conclusion is that the convection-conduction heat loss is about equal to the radiation from a surface 30 per cent black.

TABLE 6

Heat Transfers Found by Experiments under Conditions Stated (In Still Air at Atmospheric Pressure When Not Otherwise Stated). Watts per cm^2 per Degree C Difference of Temperature from Surroundings at About 300°K

No.	Name	Conditions	Watts
1		Radiation; black radiator to black surroundings	0.00068
2	MacFarlane ⁶⁶	Copper ball diam. 4 cm, to large jacket blackened inside; moist air; temperature differences 15° to 65° give about same figure	
		Polished ball, total conv., conduc., and rad.	0.00085
		Blackened ball, total conv., conduc., and rad.	0.00118
3	Langmuir ⁶⁷	Convection-conduction; vertical plane surface; temperature difference about 25°	0.00044
4	Wamaler ⁶⁸	Convection-conduction; outer surface cylindrical pipe, horizontal in large room; temperature difference about 50°	
		Pipe 9 cm diameter	0.00058
		Pipe 6 cm diameter	0.00079
5	Dickinson ⁶⁹	Convection, conduction, and radiation; ordinary cylindrical calorimeter can, 4 liter content, in jacket such that air gap is 1 cm; bright nickel surface; temperature difference about 5°	0.00030
6	Lees ⁷⁰	Convection, conduction, and radiation; nickleed bar, 2 cm in diam., suspended horizontally (?) in jacket 55 cm in diameter	0.00041
7	Harper ⁷¹	Copper spiral and jacket described in foregoing paper, i. e., large similar cylinders, 5-cm air gap all around; temperature difference 5°	
		Convection-conduction	0.00018
		Radiation	0.00012
8	Harper ⁷²	Polished copper cylinder, 10 cm diam., 10 cm high, in similar jacket of 20 cm dimensions (same as No. 7)	
		Convection-conduction	0.00022
		Radiation	0.00006
9	Soddy and Berry ⁷³	Conduction in rarefied nitrogen or oxygen for each 0.01 mm (of Hg) residual pressure, so long as mean free path of molecules is not materially less than distance between the two walls	0.00008

It becomes evident at once that in such a case as where the effective emissivity of two walls taken together is 30 per cent, no amount of pumping out the conducting gas between them can reduce the heat transfer to less than 50 per cent of its magnitude before pumping. If it be worth while to evacuate at all, for the sake of gaining this degree of thermal insulation, it must be evident that the difference between a rather poor vacuum and the very highest would be hardly appreciable so far as total heat transmitting power is concerned.

⁶⁶ MacFarlane: Proceedings Royal Society of London, 26, p. 90; 1871-2.

⁶⁷ Langmuir: Transactions American Electrochemical Society, 23, p. 299; 1913.

⁶⁸ Wamaler: Zeitschrift des Vereines Deutscher Ingenieure, 55, p. 628; 1911.

⁶⁹ Dickinson, Harper, and Osborne: This Bulletin, 10, p. 242; 1913. Surface of calorimeter 1700 cm^2 .

⁷⁰ Lees: Philosophical Magazine (5), 28, p. 458; 1889.

⁷¹ The surface of the copper spiral, while approximately that of a cylinder 10 by 10, was by no means definitely measurable as in No. 8. The agreement of the results (0.00018 and 0.00022) is satisfactory, considering all conditions. The difference in the radiation is discussed on p. 324.

⁷² Experiments described more fully on p. 327.

⁷³ Soddy and Berry: Proceedings of the Royal Society of London, A58, p. 254; 1910.

Now let us consider an emissivity that is very small, say 2 per cent black, which is perhaps the correct value for a well silvered Dewar flask. The conduction-convection is reduced to an equality with the radiation⁷⁴ (at 300° K) only when evacuation has reached the stage where the former has but one-fifteenth of its value at atmospheric pressure. It is quite worth while then to continue to the one-thirtieth stage and probably to the one-sixtieth before the radiation is so great a percentage of the total transfer (80 per cent in this instance) that the further improvement in insulation might cease to repay the trouble necessary to secure it. One-sixtieth of 0.00020 is 0.003, and from datum 9 of Table 6 the requisite vacuum is 0.0003 mm of Hg.

The two examples, 30 per cent emissivity and 2 per cent, are quite sufficient to indicate the general procedure in deciding upon a useful degree of evacuation, and the next important consideration is the probable magnitude of emissivity which will characterize various pieces of apparatus. Before passing to this topic, however, there is a supplement to Table 6 which requires a moment's attention.

WIRES

Until very recently the figures obtained experimentally for the heat loss from small wires remained uncorrelated and it is only within the last year or two that any general conclusions of value have been put forth.⁷⁵ It has, however, always been evident that the heat loss per unit area increased as the diameter of specimens was decreased, so that there was no possibility of inferring directly the correct figure for an extended surface from the loss from a small wire, yet this error has been made frequently. Taking the actual surface of the wire as the basis of the per cm² computation, Table 7 presents a few representative figures to show that the conduction-convection is very much greater than any figure quoted in Table 6. The depressed ciphers are added so as to carry the same number of figures in the two tables.

EMISSIVITIES

Turning now to the question of emissivities, only a few remarks can be made in this paper, as the subject is too comprehensive for a satisfactory digest within reasonable space.

First of all it must be borne in mind that at 300° K the wave length of maximum emission is about 10μ and the total emission

⁷⁴ Attention is directed to the fact that a Dewar flask is frequently used at temperatures where the radiation is but a small fraction of the radiation at 300° K and in such case the conclusions of this paragraph must be modified accordingly.

⁷⁵ Langmuir, loc. cit.

in the visible spectrum is an inappreciable fraction of the whole. For the reflection coefficients in the infra red it is quite usual to employ the figures given by Hagen and Rubens, as quoted in the Landolt-Börnstein tables of physical constants and from these copied into others. While these figures are no doubt excellent, they may lead to very erroneous conclusions by failure to recognize the tremendous changes in emissivity which sometimes occur for a small change in condition of surface.

TABLE 7

Conduction-convection from Wires in Still Air at Atmospheric Pressure. Watts per cm^2 per Degree Difference of Temperature from Room at 300°K

Name	Remarks	Diameter cm	Watts per cm^2 per degree
Bottomley ⁷⁶	Various sizes between limits given	0.08	0.0021 ₀
		0.04	0.010 ₀₀
Schleiermacher ⁷⁷ ..	Wire horizontal in glass tube 2.4 cm diameter	0.040	0.0033 ₀
		0.069	0.0041 ₀
Kennelly ⁷⁸	Temperature difference of about 50° . (No great difference between figures for 15° and 70°).	0.021	0.0072 ₀
		0.011	0.014 ₀₀
		0.051	0.007 ₀₀
		0.025	0.011 ₀₀
Langmuir ⁷⁹	Horizontal in room at 300°K . Same figures within 10 per cent for temperature differences 10° to 200° .	0.0126	0.017 ₀₀
		0.0069	0.027 ₀₀
		0.0040	0.046 ₀₀
Knudsen ⁸⁰	Wallaston wires	0.00042	"2000 times black ra- diation."

For illustration, consider copper, the metal most important for this paper. In such tables the reflecting power is given as over 97 per cent between 3μ and 14μ and probably averages 98 per cent in the range with which we are concerned, or the emissivity is 2 per cent. But this refers to pure copper quite free of oxide, the surface having been renewed immediately before measuring. With very slight oxidation, the least one would find on an ordinary copper surface in air, the emissivity appears to be several times greater. A copper cylinder of dimensions about the same as the overall dimensions of the spiral described in this paper radiated

⁷⁶ Bottomley: Proceedings of the Royal Society of London, 27, p. 177; 1884.

⁷⁷ Schleiermacher: Wiedemann's Annalen, 24, p. 623; 1888. Results not given in absolute measure. Assumptions made by author in deducing them may therefore possibly lead to erroneous figures.

⁷⁸ Kennelly, Wright, and Van Bylevelt: Transactions American Institute of Electrical Engineers, 28, p. 361; 1909. Figures copied from Langmuir, *Ibid.* 31, p. 1234; 1912.

⁷⁹ Langmuir: Physical Review, 24, p. 401; 1912.

⁸⁰ Knudsen: Annalen der Physik (4), 24, p. 593; 1911.

to nickered surroundings 10 per cent of the black body figure quoted, yet it was bright and not oxidized apparently. The spiral itself lost heat by radiation at a rate about 20 per cent that of a black body. Its surface also was bright and not apparently oxidized, but it must not be overlooked that the recesses at the meeting points of the layers approximate the condition for black radiation and probably increase materially the average radiation from that due to the polished copper surface not so recessed.

Wamsler⁸¹ found the emissivity of polished copper 50° above room temperature to be 18 per cent, increasing as it oxidized with heat, the increase being very rapid above 250° C. Langmuir⁸² found an emissivity of 39 per cent for "calorized" copper and 77 per cent for oxidized copper, both at 325° K.

Iron surfaces seem to show the same latitude of variation. From the table of Hagen and Rubens, 8 per cent is a fair average figure to take for the spectral interval in question. Wamsler found highly polished (wrought) iron to have an emissivity of 30 per cent, while matt oxidized surface was about the same as a black body. Langmuir found 17 per cent for bright cast iron, 50 per cent for the same oxidized.

Platinum and silver, on the other hand, seem to give more reasonably concordant results, agreeing at least in the order of magnitude. Platinum, for example, might be taken as 8 per cent from the table of Hagen and Rubens; Bottomley, reviewing Schleiermacher⁸³ quotes figures which give 10 per cent (100° C to 300° C); Bottomley⁸⁴ himself gets 13 per cent; Soddy and Berry⁸⁵ find 10 per cent (60° C to 15° C), and Knudsen⁸⁶ finds 12 per cent (100° C to 0° C).

Since the usual tables of reflection coefficients in the far infra red show few if any figures less than 90 per cent, this is sufficient cause for a rather current impression that almost any metal surface, polished to a fair degree, is a very good reflector, or low emissive power radiator, of the long heat waves. That this is by no means true is sufficiently well indicated above; indeed for a metal like copper which appears to change in emissivity so greatly for different degrees of oxidation of the surface, it would seem almost impossible to predict the radiation, and that direct experimental measurements with the surface in question would be the only means of determining it.

⁸¹ Wamsler: *Zeitschrift des Vereines Deutscher Ingenieure*, 55, p. 599; 1911.

⁸² Langmuir: *Transactions American Electrochemical Society*, 22, p. 299; 1913.

⁸³ Schleiermacher: *Wiedemanns Annalen*, 26, p. 287; 1885.

⁸⁴ Bottomley: *Philosophical Transactions of the Royal Society of London*, A178, p. 429; 1887.

⁸⁵ Soddy and Berry, *loc cit.*

⁸⁶ Knudsen: *Annalen der Physik* (4), 34, p. 593; 1911.

CONDUCTION IN RAREFIED AIR

1. HIGH VACUA. (LOW RESIDUAL PRESSURE)

When thermal insulation by employing a vacuum jacket is sought and consideration of the radiation has led to an estimate of the degree to which it is profitable to reduce the conduction, the question next in order is what degree of evacuation corresponds to a given conducting power. The answer has been anticipated by including datum 9 in Table 6, but a somewhat more full discussion is in order.

The theory of thermal conduction in highly rarefied gas has been admirably treated by Smoluchowski⁸⁷ and Knudsen⁸⁸ and can not be dwelt upon here. Soddy and Berry⁸⁹ have stated the results of their very careful measurements in a form which is very convenient of application. Their conclusions may be stated as follows: A body surrounded by a chamber which is distant from it by no more than the mean free path of the molecules of gas filling the intervening space, loses heat, in addition to the radiation, according to the law

$$\frac{dQ}{dt} = ks\theta p$$

If $\frac{dQ}{dt}$, the rate of loss of heat from the body, be in cal per sec.;

s , the area of the surface of the body, be in cm^2 ;

θ , the difference in the temperatures of the body and the surrounding chamber, be in $^{\circ}\text{C}$;

p , the pressure of the gas, be in units of 0.01 mm of Hg,

then k , the coefficient or conductivity of the gas, is a numerical constant for a considerable range of variation of the other factors entering into the relation. It is about the same for oxygen and nitrogen, numerically 2×10^{-8} , and accordingly this figure may be used for air. The law was tested for a sufficient number of pressures to establish it satisfactorily with respect to this factor, for temperature differences up to about 50° , and for a considerable number of gases, each of which was found to give a definite value for k .

A restatement of the equation in words is that each square centimeter loses 2×10^{-8} cal per sec, which is 8×10^{-8} watts, for

⁸⁷ Smoluchowski: Wiedemanns Annalen, 64, p. 101; 1898, or Philosophical Magazine (5), 46, p. 192; 1898. Kaiserlichen Akademie der Wissenschaften zu Wien, Berichte der Mathematisch-Naturwissenschaftlichen Klasse, 107, IIa, p. 304; 1898. Ibid., 108, IIa, p. 5; 1899. Philosophical Magazine (6), 31, p. 11; 1911. Annalen der Physik (4), 86, p. 983; 1911.

⁸⁸ Knudsen: Annalen der Physik (4), 84, p. 593; 1911. Ibid., 85, p. 389; 1911. Ibid., 86, p. 871; 1911.

⁸⁹ Soddy and Berry: Proceedings of the Royal Society of London, A88, p. 254; 1920. Ibid., A84, p. 576; 1911.

each degree (C) excess of temperature above that of the surrounding envelope if the intervening air be at a pressure of 0.01 mm of Hg, provided the distance separating the body and the envelope be not over 8 mm, the mean free path corresponding to 0.01 mm pressure. From this figure, 0.00008 watt per cm^2 per degree, the heat transfer by gas conduction at any other pressure lower (except for air gaps narrower than 8 mm) can be readily computed. For instance at one-eighth this pressure, or 0.0012 mm of Hg, the conduction would be the round number 0.00001 watt per cm^2 per degree, for any width of air gap up to about 7 cm.

LOW VACUA. (RESIDUAL PRESSURE "LARGE")

Since the terms high and low vacua are relative only, it will be necessary to adopt some arbitrary division and this is here taken to be the pressure at which the mean free path of the gas molecule is equal to the distance between the walls confining it. In high vacua (small residual pressure) the heat transmission is proportional to the pressure, but very soon after passing the division indicated, the increase in conduction becomes less and less for a given increase in pressure, and soon the conduction becomes constant, independent of the pressure. This condition continues to hold as the pressure is increased, probably well on beyond atmospheric pressure, but the total heat transfer is augmented by convection which becomes appreciable at a pressure which apparently varies greatly with different conditions. No doubt the shape of the surfaces plays a very important part in determining the convection, but it is unsafe to advance detailed theories. A few typical experiments are reviewed below, mainly as illustrations of the latitude in the results which have been obtained. Since almost nothing has been done yielding results in absolute measure, it is quite impossible to prepare a table of comparisons, similar to Tables 6 and 7, upon a satisfactory basis. The best which can be done is to employ some arbitrary way, as for instance by placing the heat loss due to the gas (total loss less the radiation) as unity at atmospheric pressure and comparing the fractional values of this loss at various other pressures. This is done in Table 8 by tabulating the pressures corresponding to a given fractional value of the conduction-convection loss.

A more detailed review of these experiments brings out a great many very interesting points, but as it is hopeless to reach any general conclusions of value, there would appear to be no pressing need for presenting such review here. Those interested in them are referred to the original sources which are almost all in periodicals commonly found in the better scientific libraries. The sub-

ject is one which needs further experiments carried out so that the results may be expressible in absolute measure, before generalizations can be expected.

TABLE 8

Pressure at Which Convection-conduction in Air was Found to be a Given Fraction of its Magnitude at one Atmosphere. Radiation has in Each Case been Subtracted From Total Heat Transfer

Name	Conditions	Relative conduction-convection			
		1.00	.75	.50	.25
Dulong and Petit ¹⁰	Mercury thermometer in large spherical globe.	mm of Hg 760	mm of Hg 360	mm of Hg 180	mm of Hg 45
Kundt and Warburg ¹¹	Mercury thermometer in 6-cm spherical globe.	760		150	Below 0.5
	Mercury thermometer in tall narrow cylinder.	760		Below 0.5	
Crookes ¹²	Mercury thermometer in 1½-inch spherical globe.	760	1	0.1	0.01
Brush ¹³	Mercury thermometer in large pear-shaped globe.	760	270	90	0.08
	Mercury thermometer in tall cylinder.	760	0.15	0.05	0.015
Harper	Copper cylinder, 10 cm diameter, 10 cm high in 20 by 20 jacket.	760		Above 63	0.07
Bottomley ¹⁴	0.4 mm wire in 25-mm tube	760	5	1.5	0.4
Soddy and Berry ¹⁵	Thin narrow strip in 1-cm tube	760	4	.15	0.05
Bucken ¹⁶	Fine wire in 1-mm tube	760		Below 4	

The experiments by the author have not been published elsewhere and require description sufficient to permit of a proper criticism. They were performed as preliminaries to the calorimetric measurements described in the foregoing paper, and were never intended to be separated as a properly planned investigation of the heat transmission in rarefied air; consequently there are omissions of measurements at pressures which are very desirable, and the care and time spent upon the measurements was by no means what it might have been, and the precision is not high. Nevertheless the results are certainly good to the order of magnitude (say 20 to 50 per cent, and probably very much better than this) and being in absolute measure and made with an air space of definite shape and dimensions, they may be of interest for comparison with the results of subsequent investiga-

¹⁰ Dulong and Petit: *Annales de Chimie et de Physique*, 7, pp. 225, 337; 1817. *Journal Ecole Polytechnique*, 11, p. 234; 1819.

¹¹ Kundt and Warburg: *Poggendorfs Annalen*, 156, p. 177; 1875.

¹² Crookes: *Proceedings of the Royal Society of London*, 81, p. 239; 1880.

¹³ Brush: *Philosophical Magazine* (5), 46, p. 31; 1898.

¹⁴ Bottomley: *Philosophical Transactions of the Royal Society of London*, A178, p. 429; 1887.

¹⁵ Soddy and Berry: *Loc. cit.*

¹⁶ Bucken: *Physikalische Zeitschrift*, 12, p. 1101; 1911.

tions better planned to shed light on the apparent anomalies of Table 8.

Two or more measurements were made at each of the pressures indicated in Table 9, and several series of pressures were used on different days, the agreement of the entire set being satisfactory for the purpose in view.

TABLE 9

Convection-conduction in Rarefied Air Between a Cylinder 10 cm by 10 cm and a Similar Inclosure 20 cm by 20 cm. Temperature Differences About 5°, and Mean Temperature 300° K. Watts per cm² per Degree C

Pressure in mm of Hg	760	2.30	0.77	0.24	0.12	0.083	0.046	0.024	0.016	0.014	0.003 ₂
Total watts per cm ² per degree.....	0.034	0.018	0.018	0.017 ₄	0.017	0.016	0.015	0.014	0.014	0.014	0.012
Conduction - convection.....	0.024	0.008	0.008	0.007 ₄	0.007	0.006	0.005	0.004	0.004	0.004	0.002

Later Series, Same Apparatus with Radiant Emissivity Diminished

Pressure in mm of Hg	760	63	0.014	0.009	0.0031	0.0017
Total watts per cm ² per degree.....	0.028	0.015	0.012	0.009	0.008	0.008
Conduction-convection.....	0.022	0.009	0.006	0.003	0.002	0.002

A large hollow cylindrical shell of copper was suspended in the jacket of the calorimeter described in the foregoing paper. The copper cylinder was 10 cm in diameter and 10 cm high, approximately the dimensions of the copper spiral used in the specific heat measurement described in the foregoing paper, but presenting a more definitely defined surface. It was closed at both ends, and the cylindrical wall was thick, with a constantan ribbon heating coil and sensitive platinum resistance thermometer imbedded in the copper mass but insulated from it by mica.

This cylinder was brought to a temperature about 5° above or below that of the jacket, and then the rate of cooling or warming was determined during a period of about 10 minutes, employing the resistance thermometer. From this rate, the heat capacity (1200 joules per degree), the surface (470 cm²), and the temperature difference, the total dissipation (per unit area, etc.) was calculated in absolute measure. From this total dissipation was subtracted the radiation, computed in the following manner:

The jacket being about 20 cm in diameter and 20 cm high, the air space between the copper cylinder and jacket was about 5 cm

all around, a distance which is the mean free path of a molecule of air at a pressure of about 0.002 mm of Hg. Accordingly, the figures given by Soddy and Berry⁷⁷ are applicable to the measurements made at 0.0032 mm and 0.0017 mm (Table 9), and upon computing the conduction at these pressures and deducting, the figures obtained for radiation are 0.00010 and 0.00006 watts per cm² per degree, respectively, for the two parts of Table 9. It should be noted that a very large error in the figures given by Soddy and Berry would have very little effect upon the result, provided only that the order of magnitude is correct, i. e., the conduction quite small as compared to the radiation. The process is therefore not the circle which it might appear to be at first sight. It was made necessary by reason of failure to secure a vacuum higher than indicated in the table at the times when heat transfer measurements were obtainable. The actual limit of the pump, a double-cylinder Geryk oil pump of the Fleuss type, was apparently in the neighborhood of 0.001 mm of Hg.

Pressures were measured with a McLeod gauge sensitive to about 0.0001 mm. This was connected to one pipe leading into the vacuum chamber and the pump to another, so that the apparatus was in series in the order pump, vacuum chamber, gauge, and therefore the vacuum attained was certainly as high as the gauge measurements indicated. The connecting tube was 6 mm internal diameter and not excessively long, and no great differences of temperature occurred here, so that it is not likely that the vacuum was appreciably higher than the measurements indicate. A large drying tube of phosphorus pentoxide was connected to the vacuum chamber by 15 cm of brass tubing 8 mm in diameter.

RÉSUMÉ

This chapter makes no pretense of being a thorough review of the whole subject of heat transfer in gases. It is but a note gathered from the literature and from the author's experience, attempting to set forth a little more clearly than seems to have been done elsewhere the relative magnitudes of the radiation and the convection-conduction in air at atmospheric pressure and at various stages of evacuation, for such conditions as are likely to be found in calorimetry and work with similar apparatus whether scientific or industrial.

⁷⁷ Soddy and Berry, *loc cit.*

EQUILIBRIUM IN THE SYSTEM: LEAD ACETATE, LEAD OXIDE, AND WATER, AT 25°

By Richard F. Jackson

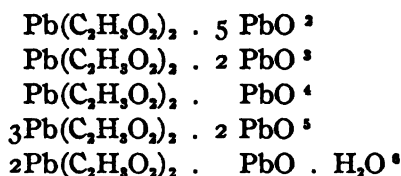
The basic acetates of lead owe a considerable importance in applied chemistry to the fact that for a large class of crude substances they are the most effective and most convenient clarifying agents known. In the analysis of crude saccharine products the question of clarification is assuming an ever increasing importance as the sugar analysis approaches a continually higher precision. In order that further advances may rest upon a firm basis, it seems highly advisable that in place of acquiring more empirical data on the crude products themselves, we turn our attention to some of the more fundamental problems involved. The present work was undertaken in order to contribute to our very meager knowledge of the basic acetates themselves and their behavior in aqueous solution. Its application to the complicated problem of sugar clarification will form the subject of a special investigation.

A glance into the history of the study of this problem reveals the fact that while a number of compounds have been reported, no work has been done in the light of modern knowledge. Much of the work which has hitherto been accepted was done under assumptions which we now know to be radically erroneous. As an instance of this the work of Löwe¹ may be cited. This investigator boiled lead oxide and lead acetate for an arbitrary length of time and upon obtaining a solution and a residue he assumed that each represented a compound. In order to identify these compounds he used them to precipitate the insoluble basic nitrate of lead which was then recrystallized before analysis. Its analysis was assumed to indicate the proportion of basic to neutral lead in the original compound. The conclusions based upon this procedure must be considered invalid.

¹ J. prakt. Chem., 96, p. 385; 1886.

In other instances investigators have attempted to isolate and purify the basic compounds and have reported the formulæ on the basis of the direct analysis of these substances. In most cases the substance obtained must have been heterogeneous. Indeed, as will appear from the present work, it is almost, if not quite, impossible to isolate at least one of the basic compounds, while the danger of obtaining a mixture is so great that it makes this method of investigation unreliable.

The following compounds have been reported:



The U. S. Pharmacopœia states that neutral lead acetate is soluble in two parts of water at 25° C. Other than this no measurement of the solubility of neutral or basic lead acetate has been made.

The present work has been intended to show what compounds exist and what are the limits of stability of each. For this purpose the problem was attacked from the standpoint of the phase rule.

PREPARATION OF REAGENTS

Lead Acetate.—Lead acetate C. P. from Baker & Adamson was recrystallized once from distilled water containing a slight excess of acetic acid. Two samples were tested by separating the lead quantitatively as sulphate and sulphide, respectively. The filtrates in each case yielded no significant residue.

Lead Hydroxide.—Recrystallized lead acetate was dissolved in water free from carbonic acid. A small quantity of this solution was added to a caustic alkali solution and the mixture allowed to stand several days to permit lead carbonate to settle. The solution was then filtered rapidly through asbestos and mixed with the

³ Wittstein and Kühn, Büchners Rep., 84, p. 181.

⁴ Löwe, loc. cit., Pelouse, Lieb. Ann., 42, p. 206; 1842.

⁵ Löwe, loc. cit.

⁶ Brown's Handbook of Sugar Analysis, p. 207.

⁷ Stolle, Handbuch für Zuckerfabriks Chemiker, p. 527; Wöhler, Lieb. Ann., 29, p. 63; 1839.

remaining lead acetate solution. The lead hydroxide precipitate was thrown on a filter and washed with water free from CO_2 , until free from sodium salts. The content of lead oxide was determined by ignition of a small sample. This procedure could not have accomplished the complete elimination of carbonate, but a few experiments showed that the presence of even a considerable amount of carbonate was without influence on the equilibrium.

Acetic Acid.—The C. P. reagent of commerce was redistilled and the middle portion of the distillate reserved for use.

ANALYTICAL PROCEDURE

The analytical processes were required to yield the percentages of neutral lead acetate and of basic lead present in the sample. These data were obtained by measuring the quantity of standard acid neutralized by the basic lead and the quantity of reagent required for the complete precipitation of lead. Two methods of estimation of total lead were utilized, namely, precipitation by normal sulphuric acid,⁷ and precipitation by one-third normal sodium oxalate.⁸

To the weighed sample in a 500-cc volumetric flask a slight excess of normal acetic acid was measured from a pipette. In the sulphate method the solution was diluted and sufficient normal sulphuric acid added for complete precipitation. The solution was made up to the calibration mark with water free from CO_2 , mixed and allowed to remain overnight. Since the total precipitate of lead sulphate amounted to more than 15 grams, the quantity remaining in solution in the presence of the excess sulphuric acid was too small to be significant. Four 100-cc aliquot portions of the clear supernatant liquid were drawn off in a pipette. Duplicate titrations were made with standard alkali to determine the excess of acid. The alkali was a solution of sodium hydroxide containing a little barium hydroxide. Phenolphthalein was used as an indicator. In the remaining two portions the excess of sulphuric acid was determined by precipitation with barium chlo-

⁷ Fresenius-Cohn: *Quantitative Chemical Analysis*, Vol. II, p. 599; 1904.

⁸ Mohr's *Lehrbuch der Chemisch-Analytische Titrimethode*, 7th Auflage, p. 798; Sutton, *Volumetric Analysis*, 10th ed., p. 245.

ride. In this precipitation the precautions recommended by Allen and Johnson⁹ were observed.

In the oxalate method the acetic acid was added in the same manner. An excess of third normal sodium oxalate was measured in and the solution made to volume, mixed, and allowed to settle. The aliquot portions of the supernatant liquid were titrated for free acetic acid with normal alkali and for excess of oxalate with potassium permanganate.¹⁰ This method, on account of its greater convenience, was the main reliance. The two methods proved to be equally trustworthy. The lead oxalate is much less soluble than lead sulphate. The presence of the slight quantity of acetic acid did not appear to increase the solubility appreciably. The acetic acid was without influence upon the permanganate titration, provided it was purified by redistillation.

The volume of the precipitate was computed in every instance and deducted from the calibrated volume of the flask. For this purpose the data of Schröder¹¹ for the density of precipitated lead sulphate are available, but no data exist on that of lead oxalate. Consequently this was determined. The precipitated oxalate was washed by decantation and transferred to a calibrated picnometer. The picnometer was nearly filled with water which was then brought to boiling in a vacuum to remove air. After adjustment and weighing, the contents of the picnometer were transferred to a gooch crucible and the weight of the dry precipitate was determined. From the data obtained the density of lead oxalate was found to be 5.28. In computing the total excess of reagent from the aliquot titer, the latter was multiplied by the ratio of the true volume of the solution to the actual volume delivered by the pipette.

Inasmuch as the computation of results was troublesome until it was condensed to routine, it is considered advisable to illustrate by specific instance the final method used.

	cc.
Total normal acid added.....	58.37
Excess of acid, by alkali titration.....	17.26
Normal acid equivalent to basic lead.....	41.11

⁹ J. Amer. Chem. Soc., 82, p. 588.

¹⁰ The procedure was that recommended by McBride, this Bulletin, 8, p. 611; 1912.

¹¹ Pogg. Ann. Erg. Bd., 6, p. 622; 1874.

$\text{PbO} = \frac{41.11 \times \frac{1}{2} \text{ M. W. PbO}}{\text{Wt. of sample (28.86g.)}}$	Per ct. 15.89
Total $\frac{N}{3}$ oxalate added	400.32
Excess oxalate, by permanganate titration	16.36
Oxalate equivalent to total lead	383.96
Ditto in normal solution	127.99
Total lead equivalent minus basic lead equivalent $127.99 - 41.11 =$	86.88
$\text{Pb (C}_2\text{H}_3\text{O}_2)_2 \text{ present} = \frac{86.88 \times \frac{1}{2} \text{ M. W. Pb (C}_2\text{H}_3\text{O}_2)_2}{\text{Wt. sample}}$	48.95

The computation from the analysis as sulphate was similar, the total added acid being the sum of the acetic and sulphuric acids.

SYNTHESIS OF BASIC ACETATES

The usual methods of preparing the basic lead acetates have consisted of boiling the neutral acetate with varying quantities of lead oxide. In the present work the compounds were made by the interaction of the neutral acetate and a suspension of lead hydroxide. These reactions were in many cases very striking, and, in contrast to the long period of boiling required in the case of the oxide, they occurred with great rapidity.

A few instances will illustrate these phenomena. In the preliminary work before the saturation curves had been located, a synthetic mixture was made up of about the composition, 20 per cent PbO and 15 per cent $\text{Pb(C}_2\text{H}_3\text{O}_2)_2$. The hydroxide was added in the form of a suspension in water. On shaking up the mixture there was an immediate solution, with the exception of a slight turbidity. Then after a few minutes the entire solution stiffened to a solid mass. This was due to the crystallization of $\text{Pb(C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbO} \cdot 4\text{H}_2\text{O}$.

Another synthetic mixture was made up of composition 20 per cent PbO, 53 per cent $\text{Pb(C}_2\text{H}_3\text{O}_2)_2$. In order to prepare a mixture containing little enough water it was necessary to dry both the neutral acetate crystals and the hydroxide suspension, the latter to a stiff paste, in a desiccator. On weighing out the components into a bottle the unmixed mass had the appearance of nearly dry solid material. After a few seconds vigorous shaking the reaction occurred rapidly and the whole mass was transformed into a mobile liquid. At the same time there occurred a very considerable absorption of heat.

THE ESTABLISHMENT AND DETERMINATION OF THE EQUILIBRIA

The equilibria were established in long narrow flasks of thin glass which were agitated in a motor-driven rotating frame under the water of a thermostat for at least 48 hours. The temperature of the bath was constant to about 0.01°C . All experiments were made at 25.00 . In order to determine with certainty whether equilibrium was reached in 48 hours the time of agitation in a number of experiments was increased by varying amounts. In these instances practically identical results within the error of experiment were obtained. (See on p. 337, experiments 7 and 8, 11 and 12, 19 and 20, 31, and 32.) Moreover, in general the times of agitation were very varied, never less than 48 hours, frequently as long as 7 days. The fact that smooth curves were obtained is further evidence that equilibrium was attained.

After the mixture had reached equilibrium the flask was placed in a rack in the thermostat to permit the solid phase to separate. In taking the sample the solution was drawn up into a pipette and a measured volume delivered into a weighed 50cc volumetric flask. The flask and substance were then weighed. This procedure gave the weight of the sample, and as the subsequent treatment was in the same flask no further transfer of material was necessary. A knowledge of the volume and weight of the solution permitted a calculation of the density. The values to three decimals are given in the table on page 337.

In studying the solid phase the indirect method of Schreinemakers¹⁹ was employed. The supernatant solution was decanted and a portion of the solid with the adhering mother liquor shaken into the volumetric flask for analysis.

¹⁹ *Zs. physik. Chem.*, 11, p. 76; Bancroft, J., *physic. Chem.*, 6, p. 179; Findlay, *Phase Rule*, 3d ed., p. 305.

Summary of Data

Experiment No.	Solution		Residue		Solid phase	Density of solution D25/4	Refractive index n_D
	PbO	Pb(C ₂ H ₃ O ₂) ₂	PbO	Pb(C ₂ H ₃ O ₂) ₂			
1.....	*-0.27	35.19			Pb(C ₂ H ₃ O ₂) ₂	1.326	
2.....	+ .10	35.60			3 H ₂ O.....	1.334	1.380
3.....	1.01	37.14				1.367	
4.....	3.38	38.93				1.422	
5.....	6.01	41.95	2.85	64.34		1.531	
6.....	9.47	44.71				1.658	
7.....	14.22	47.88	9.44	60.68			
8.....	14.44	47.92				1.852	
9.....	15.89	48.95	14.10	60.99	Transition.....		1.456
10.....	15.90	48.42	16.68	58.84	3 Pb(C ₂ H ₃ O ₂) ₂	1.930	1.456
11.....	16.25	48.85	16.63	55.52	PbO.....	1.942	1.4605
12.....	16.29	48.87			3 H ₂ O.....	1.941	
13.....	16.65	49.04				1.956	
14.....	18.83	48.71	18.61	58.98		2.024	1.467
15.....	22.23	48.52	20.50	60.05		2.161	1.4845
16.....	22.94	48.96	21.72	57.06		2.193	1.491
17.....	23.28	49.14	21.81	57.05			
18.....	23.53	49.01				2.220	
19.....	24.71	49.22	26.02	52.90	Transition.....	2.282	1.502
20.....	24.77	49.20	27.44	52.12	do.....	2.279	1.501
21.....	23.59	43.17			Pb(C ₂ H ₃ O ₂) ₂	2.048	1.469
22.....	22.78	40.78	29.14	40.39	2 PbO.....	1.951	
23.....	19.68	31.40	25.14	32.60	4 H ₂ O.....	1.657	
24.....	18.73	29.63				1.599	1.409
25.....	14.62	20.96	35.00	30.49		1.382	1.379
26.....	13.41	19.65				1.348	
27.....	10.66	12.99				1.229	
28.....	8.47	8.64				1.157	
29.....	8.08	8.07					
30.....	7.84	5.36					
31.....	7.87	5.27				1.119	
32.....	7.79	5.25				1.117	1.344
33.....	7.17	4.71			Pb(OH) ₂		
34.....	6.84	4.31				1.100	1.343
35.....	6.54	4.25	68.60	1.39		1.095	
36.....	5.91	3.82				1.085	1.340
37.....	5.29	3.40				1.075	
38.....	.20	.11					

*Acidity expressed in terms of PbO.

THE SOLID PHASES

As a study of the diagram opposite page 338 will reveal, there are four solid phases which can exist in equilibrium with aqueous solutions of the two solid components.

The *neutral lead acetate* $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ consists of brilliant monoclinic prisms. It can exist in equilibrium with an aqueous solution containing dissolved substance of its own composition. It is also capable of existence in equilibrium with solutions containing as much as 15.9 per cent basic lead, estimated as oxide. Its saturation curve AB is continuous with one extending into acid solutions. The solubility of the neutral acetate in neutral solution is, by interpolation between experiments 1 and 2, 35.50 per cent.

The *tetra-lead-monoxy-hexacetate*¹⁸ $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO} \cdot 3 \text{H}_2\text{O}$ consists of thin plates which may attain a diameter of 5mm, but which usually appear as small lustrous silky crystals whose form is difficult to recognize. It is exceedingly soluble in water and forms solutions of density, 1.93 to 2.28. It can not exist in equilibrium with aqueous solutions of itself, but depends upon an excess of dissolved basic lead. On account of the small size and softness of the crystals and the high density and viscosity of the mother liquor, it is practically impossible to isolate in pure form. It is probable that these experimental difficulties are responsible for the fact that its composition has not previously been correctly ascertained. To establish the formula of this compound six lines were determined. These gave rise to a large number of intersections, of which 10 were at sufficiently large angle to be considered representative of the solid phase. The mean of these 10 was the accepted value.

	Calculated for $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO} \cdot 3 \text{H}_2\text{O}$	
	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	H_2O
Calculated	77.9	4.2
Found	77.9	4.3

The apparent precision of the accepted value is somewhat deceptive, as the individual determinations are slightly scattering.

The *tri-lead-dioxy-diacetate* $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{PbO} \cdot 4 \text{H}_2\text{O}$ has been isolated previously and its formula, with respect to the two solid components, correctly ascertained. It has been hitherto described as an amorphous solid, and in fact, as it usually occurs it has that appearance. Nevertheless, by slow evaporation of its clear solu-

¹⁸ For nomenclature, see Hoffman, Dictionary of Inorganic Compounds, 1, p. 44.

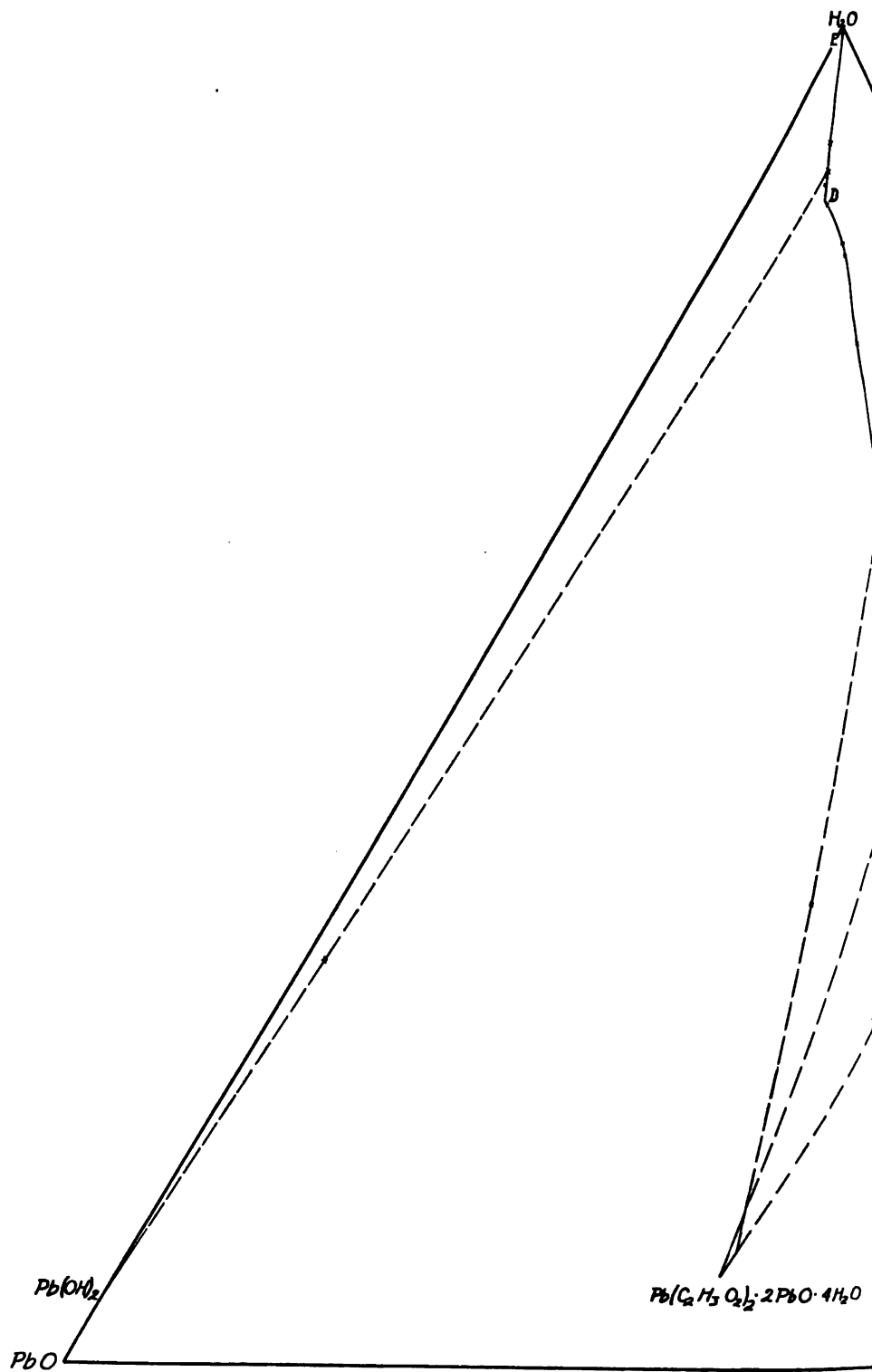
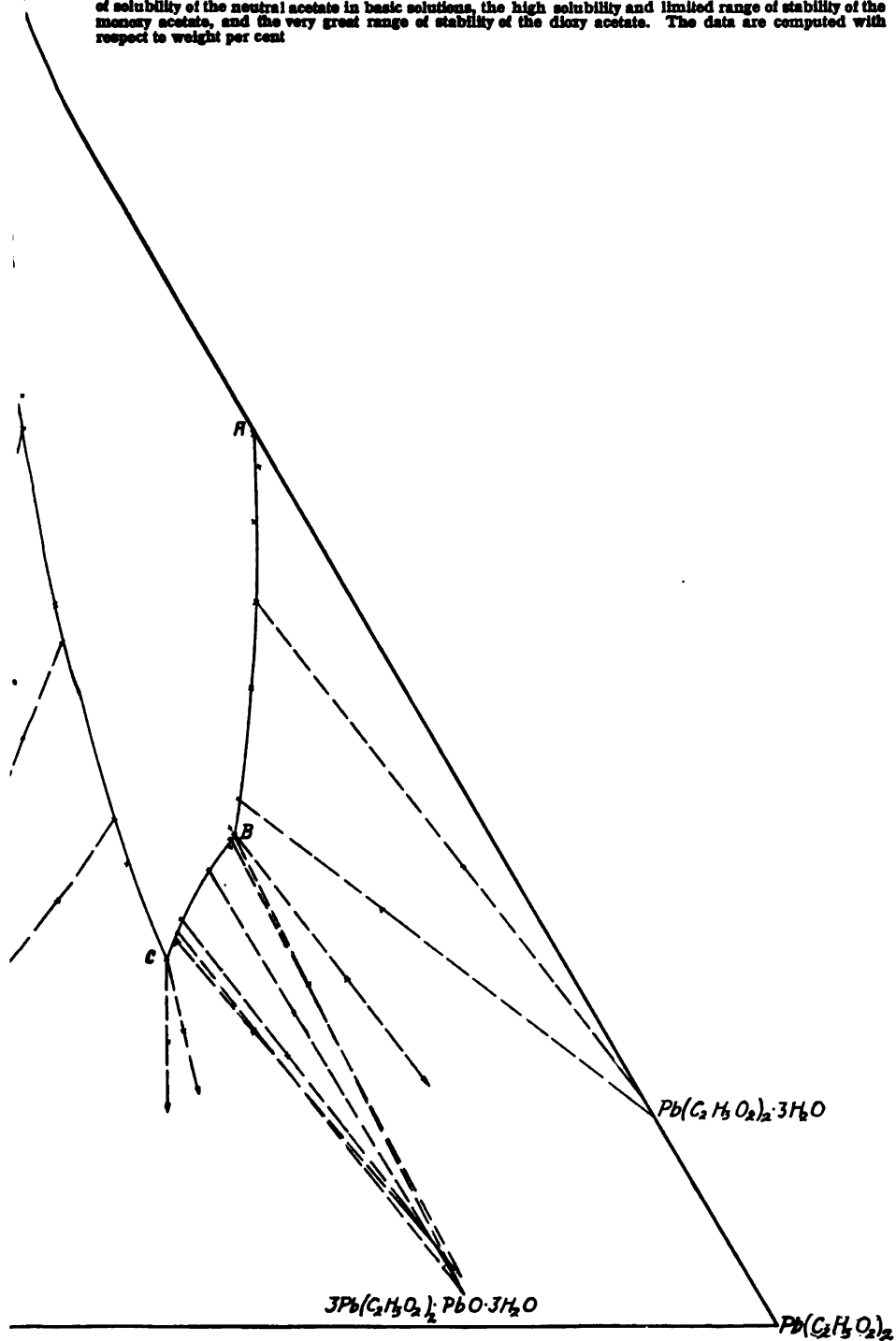


FIG. 1.—*Isothermal equilibrium at 25°*

The curves AB, BC, CD, and DE represent the composition of the solution in equilibrium with the respective solid phases. The area ABCDE encloses the region of unsaturated solutions. Note the great increase of solubility of the neutral acetate in basic solutions, the high solubility and limited range of stability of the monox acetate, and the very great range of stability of the dioxy acetate. The data are computed with respect to weight per cent



tion it can be obtained in small rather ill-formed needles which leave no doubt of its crystalline character. Its saturation curve CD has a very great length, extending from 13 per cent to 74 per cent of dissolved substance. It is stable in equilibrium with aqueous solutions of itself.

	Calculated for $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbO} \cdot 4 \text{H}_2\text{O}$	
	PbO	H ₂ O
Calculated	52.9	8.55
Found	52.5	8.6

Lead hydroxide. $\text{Pb}(\text{OH})_2$ is in equilibrium with solutions containing less than 5 per cent of lead acetate.

THE QUADRUPLE POINTS

At 25° there are three sharply defined quadruple points. The transition mixture at B (p. 338) was obtained by approaching it with successive additions of neutral acetate to the solution of the monooxy acetate.

The transition mixture at C was reached in two separate experiments, one a new synthetic mixture which was filtered and allowed to concentrate in a desiccator, the other a mixture formed by addition of neutral lead acetate to a solution which was on the saturation curve CD. The solutions proved to be of identical composition, while the solid phases, as shown by the arrows, were mixtures in different proportions of the two solid phases in equilibrium with the two intersecting saturation curves.

At the point D the dioxy acetate and lead hydroxide can exist in contact with the same solution.

THE SATURATION CURVES

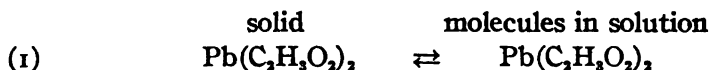
The saturation curves in equilibrium with the four respective solid phases are in some respects noteworthy. The curve AB, representing the solubility of neutral lead acetate in basic solutions, shows a remarkably high rate of increase of solubility of the solid phase. In order to cause such a rise in solubility there must occur a more deep-seated change in the solution than the mere admixture of two solutes. The curve is slightly convex toward the solid phase. The curve BC is approximately a straight line. The

solution contains a nearly constant quantity of lead acetate with varying lead oxide content. Since the dioxy acetate has a low temperature coefficient of solubility and the neutral acetate a high one it is conceivable that at some temperature in the neighborhood of 0° this small curve would be squeezed out of existence. At such temperature we should have three solid phases in equilibrium with the same solution and vapor and hence a nonvariant point. The curve CD in equilibrium with the dioxy acetate shows again the great effect upon the solubility which a relatively slight change in the ratio of basic to neutral lead exerts. It is slightly concave toward the solid phase. The curve DE is practically linear.

The plot opposite page 338 was constructed with reference only to weight percentages. If the data are plotted in molecular percentages, a diagram of the same general form results, but of very much diminished area. On account of the high molecular weight of the lead compounds the molecular percentages become very low.

A study of the purely chemical equilibria enables us to understand some of the changes which occur in the solution and thus to predict in some measure the course of the saturation curves.

Starting at the point A of the diagram opposite page 338, we find neutral lead acetate crystals in equilibrium with a solution of neutral lead acetate. We may suppose that the first equilibrium is between whole molecules thus:



neglecting the water of hydration.

Undoubtedly the dissolved salt is then to some extent both ionized and hydrolyzed. However, it must be equilibrium (1) which determines the solubility of the crystals and the constant of that equilibrium must be maintained whatever subsequent reactions occur.¹⁴

Upon addition of lead hydroxide the first basic acetate which makes its appearance has the formula $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO} \cdot 3\text{H}_2\text{O}$. The solution does not become saturated with respect to the solid phase until about 15 per cent of lead oxide is dissolved. Here, again, an equilibrium between whole molecules of solid and dissolved basic acetate must exist. The solution represented by the

¹⁴ This must be rigorously true for minute changes in the solution.

saturation curve AB of the neutral acetate must also contain this same molecular species, although in a state of unsaturation. There must then be in the solution an equilibrium between the dissolved molecules of neutral acetate and those of the monoxy acetate, thus—



Now, from this equation it appears that one molecule of lead hydroxide causes the disappearance of three molecules of neutral acetate. The equation would occur almost totally from left to right at the low concentrations of the basic acetate. If, then, we add lead hydroxide to a saturated solution of the neutral acetate, we cause a disproportionately large quantity of dissolved lead acetate molecules to disappear. But now the original equilibrium between the neutral crystals and the dissolved neutral molecules must be maintained, hence a large quantity of neutral acetate must go into solution. This would account for the astonishing increase of solubility of the neutral acetate in basic solutions.

Of interest in this connection is the correlation of another phenomenon. Parsons¹⁸ has shown that the freezing point of a lead acetate solution is raised by the addition of basic lead even although more solid substance is in solution. In his discussion he very justly pointed out that no evidence of a molecular complex then existed. If, however, equation (2) is substantially correct, the addition of one molecule of lead hydroxide to three of acetate has caused the formation of but one molecule of the basic compound, or a disappearance of three molecules. Since the lowering of freezing point depends only upon the number of dissolved particles, we should expect a rise and not a lowering upon the addition of basic lead.

If we may make the assumption that the constancy of equilibrium (1) is rigidly maintained throughout the wide variation of conditions represented by the curve A B, we can make a further prediction in regard to the saturation curve. If we continue the addition of lead hydroxide, the concentration of the basic acetate continually increases, and gradually equation (2) becomes important in the sense from right to left. Thus, at the farther end of the curve the addition of a small quantity of lead hydroxide must

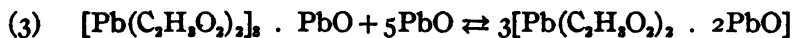
¹⁸ J. Physic. Chem., 11, p. 659; 1907.

produce a smaller relative effect than at the low concentrations. In other words, the saturation curve should have, according to this theory, the convex shape which was found by experiment.

The nature of the solution represented by AB undergoes some variation between A and B in respect to basicity, viscosity, and density, and it seems at first somewhat violent to assume the constancy of equation (1). On the other hand, if we calculate in molecular per cent instead of weight per cent we find that the point A corresponds to but 2.98 per cent lead acetate and the point B to 6.93 per cent lead acetate and 3.28 per cent lead oxide. As far as molecular percentages are concerned we are still dealing with fairly dilute solutions. This justifies to some extent our assumption.

The mechanism of the reactions can not be supposed to be as simple as represented by equation (2), but even so, we may say with certainty that the end members of the chain of reactions are just as represented, namely, neutral lead acetate molecules and basic lead acetate molecules, and whatever reasoning has been applied would be equally valid if the mechanism of the reaction included the products of ionization and hydrolysis.

With regard to the second saturation curve BC, viz, that in equilibrium with the solid phase $[\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2]_s \cdot \text{PbO}$, let us suppose we are following the curve from right to left. Neutral lead acetate has now acquired so great a solubility that the basic acetate is the more insoluble substance and separates from its own saturated solution. As we continue to add lead hydroxide the following reaction becomes important:



Here it requires five molecules of lead hydroxide to cause the disappearance of one molecule of the monooxy acetate and we should expect just what happens experimentally—a much slower increase of solubility of the solid phase with continued addition of lead hydroxide. Furthermore, since the dioxy acetate is a relatively insoluble substance it must reach its saturation after a relatively small addition of lead hydroxide. As we pass down the saturation curve BC of the solid phase $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO}$ we

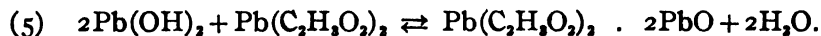
gradually increase the concentration of the dioxy acetate, namely, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbO}$, until at the quadruple point C we increase it to its saturation point and it begins to separate. Further addition of lead hydroxide converts the soluble monoxy acetate into the relatively insoluble dioxy acetate, which immediately precipitates. Hence occurs the very rapid decrease of solubility as shown by the saturation curve CD.

The convexity of the curve CD may be explained if we make assumptions similar to those made with the curve AB. Let us start with the transition point D and approach C. This can be accomplished by adding neutral lead acetate to the saturated solution of the dibasic acetate. The reaction is then



The increase of solubility would according to our theory depend upon the disappearance of the dissolved dioxy acetate and the appearance of the very soluble monoxy acetate. At first the concentration of the monoxy acetate is low and the reaction proceeds almost entirely in the sense of the equation from left to right. As the concentration of monoxy acetate increases the former reaction is opposed by the reverse equation, and consequently the rate of increase of solubility diminishes. Thus the convexity toward the solid phase.

The slope of the saturation curve DE of lead hydroxide possesses some interest. Upon adding lead acetate the following reaction occurs:



Since with lead hydroxide as the solid phase we are far from the region of stability of the neutral acetate, the latter can not remain in considerable concentration, and since the hydroxide itself has but slight solubility, we should expect the dissolved substance to consist almost entirely of the dioxy acetate. In this compound the weight ratio of lead acetate to lead oxide is 0.73, while in the solution of the curve DE it is 0.64. This indicates a slight excess of dissolved lead hydroxide which apparently acquires an increased solubility in solutions of basic acetates.

If this latter conclusion is correct, reaction (5) will continue in the sense from left to right even after the point D has been passed and the solid phase has changed from the hydroxide to the dioxy acetate. During the initial stages of the curve DC the addition of neutral acetate results only in an exhaustion of this dissolved hydroxide and makes no demands upon the dioxy acetate. Consequently, reaction (4) does not become predominant until lead hydroxide is exhausted. As a result of this we find at the upper end of CD a slight but unmistakable change of curvature.

In conclusion, it is a pleasure to acknowledge the kind assistance rendered by Dr. William Blum of this Bureau, who made many valuable suggestions in regard to analytical procedure, and by Dr. John Johnston, who read the manuscript critically.

SUMMARY

1. The analysis of basic lead acetate was performed by measuring the volume of standard acid neutralized by the basic lead and the volume of reagent required for the complete precipitation of lead.

2. The synthesis of the basic acetates was accomplished by the interaction of lead acetate and lead hydroxide. Some of the accompanying phenomena are described.

3. A theory of the course of the saturation curves is proposed.

4. The solid phases capable of existence are:

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ brilliant monoclinic crystals. It can exist in equilibrium with acid and neutral solutions and with basic solutions containing as much as 15.8 per cent lead oxide. Its solubility in water is 35.50 per cent.

$3 \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO} \cdot 3 \text{H}_2\text{O}$ crystallizes in plates. It is exceedingly soluble in water and forms solutions of density 1.93 to 2.28. The substance is unstable in solutions of itself. For its existence in equilibrium with a solution there must be an excess of dissolved basic lead. The solutions contain at the extremes of the saturation curve 15.89 per cent PbO , 48.95 per cent $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and 24.74 per cent PbO , 49.21 per cent $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2 \text{PbO} \cdot 4 \text{H}_2\text{O}$ consists of needles which may be so small as to seem amorphous. It is capable of existence in contact with solutions of itself but under such conditions has a

solubility of but 13.3 per cent. Its saturation curve possesses a very great length. The extremes of solubility are 7.4 per cent PbO, 4.8 per cent $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, and 24.74 per cent PbO, 49.21 per cent $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

$\text{Pb}(\text{OH})_2$ is stable in equilibrium with solutions containing as much as 7.4 per cent PbO and 4.8 per cent $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.

WASHINGTON, August 19, 1914.

NOTE: Since the electrotyping of the foregoing article, another reference to previous work was discovered in Watt's Dictionary of Applied Chemistry under the caption, "Acetic Acid." The work was that of Plöchl (Berichte, 13, p. 1647) in 1880. The author describes the compound $\text{Pb}_2(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{OH}$, which is probably identical with the monoxy acetate $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO} \cdot 3 \text{H}_2\text{O}$ described above. He states that it may be prepared by repeatedly drenching the normal acetate with absolute alcohol. It is curious that this work has almost entirely escaped notice in subsequent reviews of the subject of the basic lead acetates.

A WATTHOUR METER METHOD OF TESTING INSTRUMENT TRANSFORMERS

By P. G. AGNEW

Attempts to determine the constants of instrument transformers by using wattmeters or watthour meters in both the primary and secondary circuits have not met with much success. Modern transformers have such good characteristics that the small differences to be measured are more or less masked by the unavoidable errors of measurement. Moreover, such a method is not applicable to high voltage or large current ranges, which are commercially the more important.

Modern induction watthour meters can, however, be used to determine the *difference* in ratios, and also the *difference* in phase angles of either two voltage transformers or of two current transformers, provided the two transformers are of the same range. If, then, the ratio and phase angle of one of the transformers are known, it may be treated as a standard transformer and the constants of other transformers determined in terms of the constants of the standard.

Several modifications of the potentiometer method are available for the precise determination of ratio and phase angle, for the most part making use of laboratory instruments.¹

OUTLINE OF METHOD

For voltage transformers an auxiliary current is passed in series through the current coils of the two meters, which are duplicates, and the voltage coil of each meter is connected to one

¹Agnew and Fitch, this Bulletin, 6, p. 282, 1909, Reprint No. 230; Electrical World, 54, p. 2042, 1909. E. Orlich, ETZ, 30, p. 435, 466, 1909. L. T. Robinson, Trans. Amer. Inst. Elec. Eng., 28, p. 1005, 1909. F. A. Laws, Elec. World, 55, p. 223, 1910. Sharp and Crawford, Trans. Am. Inst. Elec. Eng., 29, p. 1517, 1910. Agnew and Silsbee, Proc. Am. Inst. Elec. Eng., 31, p. 1267, 1912. Schering and Alberti, Archiv für Elektrotechnik, 2, p. 263, 1914. A method of testing voltage transformers adapted to central-station use and requiring only portable instruments has been described by Brooks, this Bulletin, 10, p. 419, 1914, Reprint No. 227; Electrical World, 62, p. 898, 1913.

of the transformers. If the meters were adjusted to precisely the same rate, the ratios of the transformers would be inversely proportional to the number of rotations of the meters in a given time. Practically the meters can not be adjusted to precisely the same rate, but the difference in rates may be eliminated by interchanging the meters.

The difference in the phase angles may also be obtained by changing the phase of the auxiliary current so that the meters are working on low power factor, since this difference in phase makes the meters run at different speeds as they are connected to one or

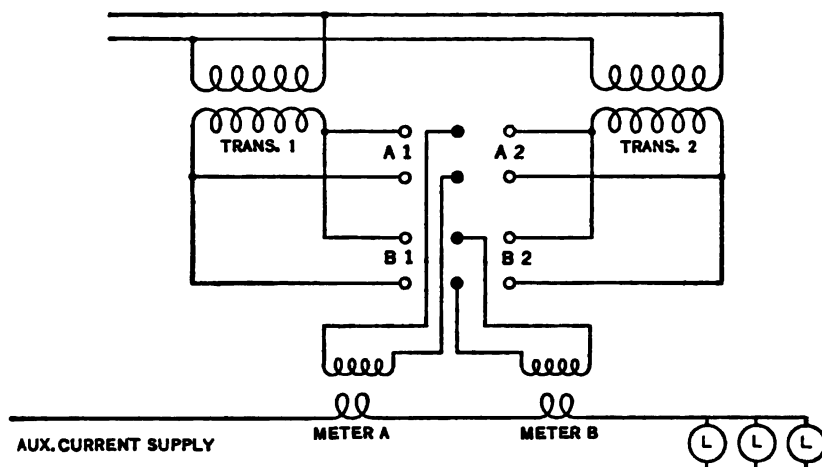


FIG. 1.—Arrangement for testing voltage transformers

the other of the transformers. From this data and a knowledge of the difference in ratios obtained at unity power factor the difference in phase angles can be calculated. A diagram of connections for testing a voltage transformer by this method is shown in Fig. 1. The ratio measurement may be carried out with a single-phase source of supply. If a three-phase source is available, it is convenient to use a lamp bank for the auxiliary current, putting it on the same phase with the transformers for the ratio measurement and on either of the other phases for the phase angle measurement.

Fig. 2 shows the arrangement of circuits for testing current transformers. The use of the current and the voltage coils of the

meters is inverted in respect to their use in the case of the voltage transformer. The primaries of the current transformers are in series, and the current coils of the two meters are connected alternately to the two transformers. An auxiliary voltage is applied to the voltage coils of the meters. Otherwise the tests are carried out in the same way as for the voltage transformer.

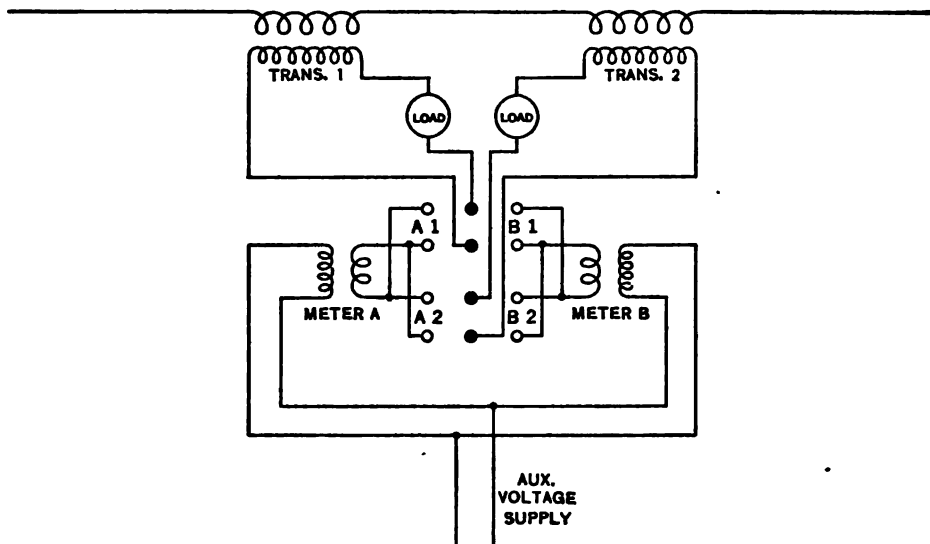


FIG. 2.—Arrangement for testing current transformers

Let m_a , m_b = the rates of the two meters (the rate being the ratio of the recorded watthours to the true watthours).

k = the disk constant of the meters (nominal watthours per revolution).

R_1 , R_2 = ratios of transformers.

α_1 , α_2 = phase angles of transformers (positive for the secondary leading opposition to the primary).

a_1 , a_2 = number of turns made by meter A when connected to transformers 1 and 2, respectively.

b_1 , b_2 = the same for meter B.

$\cos \theta$ = power factor.

Consider the case of a meter connected to a voltage transformer, and working on low power factor, current lagging. In making t

turns a meter records tk watt hours. Taking into account only the rate of the meter, m , and the ratio of the transformer, R , this gives for the energy represented by the primary voltage and the auxiliary current $\frac{tk}{m} R$. But the meter is working at a power factor of $\cos(\theta + \alpha)$ instead of $\cos \theta$, and hence the expression for the energy finally becomes

$$\frac{tkR \cos \theta}{m \cos(\theta + \alpha)}$$

or

$$\frac{tkR}{m \cos \alpha (1 - \tan \alpha \tan \theta)}$$

or, since α is very small and hence its cosine may be taken as unity,

$$\frac{tkR}{m (1 - \tan \alpha \tan \theta)} \text{ approximately.}$$

Applying this to a set of readings taken by interchanging the meters on the transformers

$$\frac{a_1 k R_1}{m_a (1 - \tan \theta \tan \alpha_1)} = \frac{b_2 k R_2}{m_b (1 - \tan \theta \tan \alpha_2)} \quad (1)$$

$$\frac{a_2 k R_2}{m_a (1 - \tan \theta \tan \alpha_2)} = \frac{b_1 k R_1}{m_b (1 - \tan \theta \tan \alpha_1)} \quad (2)$$

from which it may easily be shown² that

$$\frac{R_2}{R_1} = \sqrt{\frac{a_1}{a_2} \cdot \frac{b_1}{b_2}} \quad (3)$$

² From (1) and (2)

$$\frac{a_1}{a_2} \cdot \frac{R_1}{R_2} \cdot \frac{1 - \tan \theta \tan \alpha_2}{1 - \tan \theta \tan \alpha_1} = \frac{b_1}{b_2} \cdot \frac{R_2}{R_1} \cdot \frac{1 - \tan \theta \tan \alpha_1}{1 - \tan \theta \tan \alpha_2} \quad (A)$$

which reduces to equation (3) for unity power factor. Since the products of the tangents in (A) are small, it may be written approximately

$$1 + s \tan \theta (\tan \alpha_1 - \tan \alpha_2) = \frac{a_2}{a_1} \cdot \frac{b_1}{b_2} \left(\frac{R_2}{R_1} \right)^2$$

from which (4) immediately follows.

(5) may be obtained from (3) by noting that the latter may be written in the form

$$\frac{R_2}{R_1} = \sqrt{\left(1 + \frac{a_1 - a_2}{a_2}\right) \left(1 + \frac{b_1 - b_2}{b_2}\right)}$$

or

$$\frac{R_2 - R_1}{R_1} = \frac{1}{2} \left(\frac{a_1 - a_2}{a_2} + \frac{b_1 - b_2}{b_2} \right) \text{ approximately.}$$

which is equation (5).

Similarly (4) becomes

$$\begin{aligned} \tan \alpha_2 - \tan \alpha_1 + \frac{1}{s \tan \theta} \left[1 - \left(1 + \frac{a_2 - a_1}{a_1} \right) \left(1 + \frac{b_2 - b_1}{b_1} \right) \left(1 + \frac{R_2 - R_1}{R_1} \right)^2 \right] \\ = -\tan \alpha_1 + \frac{1}{\tan \theta} \left[\frac{a_1 - a_2}{2a_1} + \frac{b_1 - b_2}{2b_1} - \frac{R_2 - R_1}{R_1} \right] \text{ approximately.} \end{aligned} \quad (B)$$

Since there are 3438 minutes in a radian (B) reduces to (6).

where the a 's and b 's are readings taken at unity power factor, and that

$$\tan \alpha_2 - \tan \alpha_1 = \frac{1}{2 \tan \theta} \left(1 - \frac{a_2}{a_1} \cdot \frac{b_2}{b_1} \cdot \frac{R_2^2}{R_1^2} \right) \quad (4)$$

where the a 's and b 's are now readings taken at low power factor.

(3) is the general formula for the ratio R_2 in terms of the ratio R_1 , and (4) is the general formula for the phase angle α_2 in terms of α_1 and the ratio of the ratios.

These may easily be put into convenient form for slide rule computation by making a few allowable approximations,³ giving for the difference in ratios expressed as a fraction of the ratio of the standard transformer

$$\frac{R_2 - R_1}{R_1} = \frac{1}{2} \left[\frac{(a_1 - a_2)}{a_2} + \frac{(b_1 - b_2)}{b_2} \right] \quad (5)$$

and for the phase angle

$$\alpha_2 (\text{in minutes}) = \alpha_1 + \frac{3438}{\tan \theta} \left[\frac{a_1 - a_2}{2a_1} + \frac{b_1 - b_2}{2b_1} - \frac{R_2 - R_1}{R_1} \right] \quad (6)$$

Equations (5) and (6) are the working formulas for ratio and phase angle, respectively, and may ordinarily be used instead of the more exact formulas (2) and (3). The approximations involved will amount to less than 0.1 per cent in ratio for differences in the formula not exceeding 3 per cent, and to less than 0.01 per cent in ratio for differences not exceeding 1 per cent.

Equation (6), which gives the phase angle, has its signs correct for voltage transformers connected to meters working on lagging current, and for current transformers connected to meters working on leading current. If the conditions are vice versa, the + sign before the bracketed expression should be changed to -. However, it may often be more convenient not to depend upon this relation, but to use the following facts as criteria to experimentally determine whether the transformer under test has a greater or a smaller phase angle than the standard transformer:

1. Adding a noninductive load to a voltage transformer always tends to lag the secondary voltage.
2. Adding noninductive resistance in the secondary of a current transformer tends to advance the phase of the secondary current.

EXPERIMENTAL RESULTS³

Fig. 3 shows the results of the test of a 5500/110 volt transformer by means of two watthour meters and another transformer used as a standard, compared with the results of a precision laboratory method.⁴ The full lines represent the results of the laboratory method and the isolated points those of the watthour meter

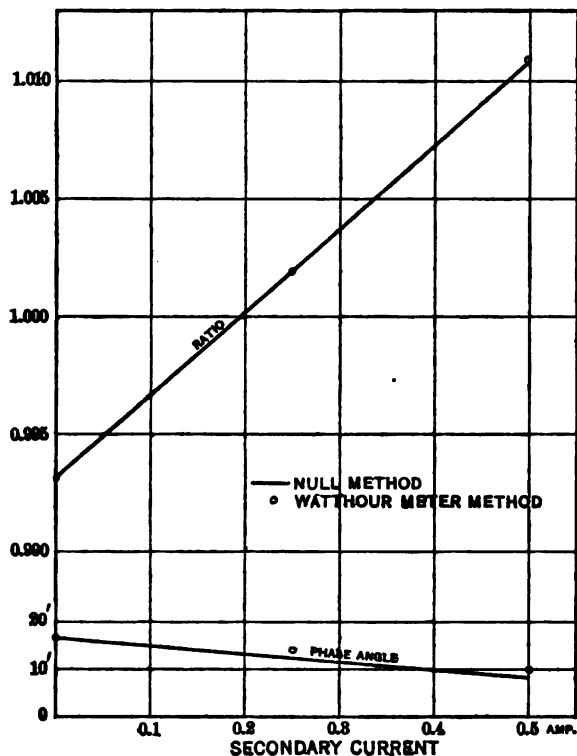


FIG. 3.—Ratio and phase angle of voltage transformer—comparison of watthour meter method with null method

method. Each point is the average of two runs of 100 turns each, and readings were taken to 0.01 turn.

Similarly, Fig. 4 shows the results of a comparison of the two methods for a 25 to 5 ampere current transformer. Each point is

³ The author is indebted to W. H. Stannard for assistance in the experimental work.

⁴ Agnew and Silsbee, Proc. Am. Inst. Elec. Eng., 31, p. 1267, June, 1912.

here also the average of two runs of 100 turns each, excepting at the lower currents where fewer turns were taken.

The meters used were of the type known commercially as K_s , the disks of which had been graduated in hundredths of a revolution.

It will be seen that the accuracy obtained is greater than is required in commercial power measurements. The method is easily capable of determining ratio to 0.02 or 0.03 per cent, and phase angle to one or two minutes.

It has been found possible to more than double the speed of the meters by shunting the magnets by small pieces of soft iron and

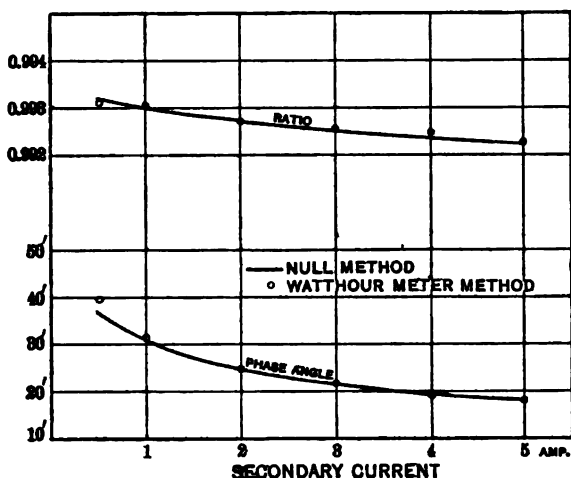


FIG. 4.—Ratio and phase angle of current transformer—comparison of watt-hour meter method with null method

yet get equally accurate results. It is not generally realized that under the very best conditions modern induction meters will repeat consecutive runs to a precision of about 0.01 per cent at full load. This is clearly shown by the following observations taken with the meters in parallel on the same load. The tenths of a division (thousandths of a revolution) were estimated in taking readings. The speed of the meters had been increased to double normal value by shunting the magnets.

Run	Per cent of full load	Number of turns	
		Meter A	Meter B
1.....	100	100	100.126
2.....	100	100	.123
3.....	100	100	.124
4.....	100	100	.127
5.....	100	100	.140
6.....	100	100	.135
7.....	100	100	.136
8.....	10	10	10.063
9.....	10	10	.067
10.....	10	10	.061
11.....	10	10	.068
12.....	10	10	.066

OVER-ALL CORRECTIONS FOR RATIO AND PHASE ANGLE

There are cases in which it may be convenient to obtain a lump correction for both ratio and phase angle rather than to determine them and to correct for them independently. For example, take the case of a watthour meter and current transformer metering the power supplied to an induction motor. If the standard transformer is inserted in series with the line and readings taken at whatever power factor the system is operating under, then we may consider R_s in either of equations 3 or 5 as the combined or over-all power ratio of the transformer. To carry this out in routine work, it would practically be necessary to have a set of curves for the standard transformer giving this ratio calculated from ratio and phase angle for various power factors.⁵ Yet,

⁵ A discussion of the calculation of the errors introduced by the phase angles of instrument transformers is given by L. T. Robinson, *Trans. Am. Inst. Elec. Eng.*, 28, p. 1005, 1909. Corrections are tabulated for various power factors and phase angles. Similar tables are given in the *Meter Code*, p. 125, 1912, and in the *Meterman's Handbook*, p. 296, 1912.

The matter may be put very briefly in the form

$$\text{True watt hours} = 1 + \tan(\alpha_s - \alpha_v) \cdot \tan\theta \times \text{apparent watthours}$$

where α_s and α_v are the phase angles of the current and voltage transformers respectively, being positive for the reversed secondary (current or voltage) leading the primary. That the correction factor takes this form, with but a slight approximation may be seen from the reasoning used in the text in deducing equations 1 and 2. θ is to be counted positive for current leading and negative for current lagging. For example, if we have only a voltage transformer whose reversed secondary voltage lags 20' behind the primary voltage, and if the power factor of the load is 0.5, current lagging, the correction factor due to phase angle is

$$\begin{aligned} [1 + \tan\{0 - (-20')\} \tan(-60^\circ)] &= [1 + (+0.0058)(-1.73)] \\ &= [1 - 0.0100] \end{aligned}$$

or 1.0% is to be subtracted from the reading.

since these curves would be computed once for all, for the standard transformer, it would obviate the necessity of going through a somewhat complicated computation for each transformer tested. Of course a similar method could be developed for the case of the voltage transformer, but the complications involved would hardly make it worth while for the voltage transformer alone. In fact, good voltage transformers, at least at 60 cycles, have such small phase angles that in most work the errors introduced by them is no greater than the uncertainty due to other causes.

This process may be extended to the case in which both current and voltage transformers are used. For such a test one meter would be connected to both of the standard transformers (current and voltage), the other to both the transformers under test. Either of equations 3 or 5 will in this case give the over-all power ratio of the two transformers under test (R_2), for the given condition in terms of the corresponding over-all ratio for the two standard transformers (R_1). This latter quantity could be taken from curves calculated for the two standard transformers, as mentioned above. Experimentally the process is simpler than would appear at first sight since no auxiliary current or voltage is required. This method should prove useful in checking transformers used in the metering of large blocks of power, either single phase or 3 phase.

MISCELLANEOUS DETAILS

The use of two of the portable watthour meters so largely used in meter testing is much more convenient than that of house type meters with graduated disks, as the trouble of counting turns is eliminated. However, for economy of time in testing current transformers rated at 5 amperes secondary current, a 5-ampere watthour meter is preferable to one of a 10-ampere range, as the length of time required for a test with a given accuracy is roughly only half as great. In general, a 1 or 2 ampere range can not be used on the light loads, as the impedance which would be introduced in the secondary of the transformer would be prohibitive.*

* For the same design a 2-ampere instrument has as much impedance as six 5-ampere instruments, and a 1-ampere instrument has as much impedance as twenty-five 5-ampere instruments.

Of course, in the case of a voltage transformer the range is immaterial, as the current is an auxiliary one.

In testing current transformers it is very convenient to use as a source of current a step-down transformer giving but a few volts on the secondary but having ample secondary current capacity. But in such an arrangement if the resistance in the secondary circuit is very low the current may lag very appreciably behind the voltage. This will produce a small error in the ratio measurement, but such a condition is readily detected by the measuring instruments in the circuit. The best way to overcome this difficulty is by the use of a phase-shifting transformer as a source of the auxiliary voltage. Such a transformer is of very great utility for many other purposes, such, for example, as testing meters at low power factor. If such a device is not available, the error may be eliminated by a process of successive approximation. To do this, compute ratio and phase angle from the data just as if the ratio had been determined at unity power factor, and compute the phase angle at whatever power factor the instruments show. Let these be R'_2 and α'_2 , and suppose the power factor in the ratio measurement was $\cos \theta_0$ instead of unity. By applying equations 5 and B to this case, using θ_0 instead of θ , a little consideration will show that

$$\tan \alpha'_2 = \tan \alpha_1 + \frac{1}{\tan \theta_0} \left[\frac{R'_2 - R_1}{R_1} - \frac{R_2 - R_1}{R_1} \right]$$

which may be solved for R_2 ,

$$R_2 = R'_2 - R_1 \tan \theta_0 (\tan \alpha'_2 - \tan \alpha_1)$$

With this second approximation to the value of R_2 , we may recompute α_2 .

Care must be used never to open the secondary circuit of a current transformer while current is passing through the primary, for if this is done the properties of the iron will be altered and the ratio and phase angle increased.⁷ In case a transformer is accidentally open circuited it may be brought back to its normal condition by carefully demagnetizing.

It is well to open both current and voltage circuits of the meters at the end of a run, as some meters are more apt to creep on current alone than on voltage alone.

⁷ Agnew and Fitch, this Bulletin, 6, p. 597, 1909, Reprint No. 130.

It is important that the ratio and the phase angle of the standard transformer, whether of the current or voltage type, be determined under actual working conditions of load, including the meter. Multiple-range transformers are very convenient as standards and good transformers have very accurately the same constants for the different series-parallel arrangements of coils. If the no-load ratio of a voltage transformer is required, it may be obtained very closely by adding a second or duplicate meter as load, and then extrapolating to the no-load condition.

While the present method has neither the high precision nor the elegance of the null laboratory methods, it has ample accuracy for commercial requirements, it is independent of ordinary line fluctuations, and no specialized apparatus is required.

WASHINGTON, July 18, 1914.

INSULATING PROPERTIES OF SOLID DIELECTRICS

By Harvey L. Curtis

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I. INTRODUCTION

For many years physicists, electrical engineers, and others using electrical apparatus have felt the need of some material to replace the hard rubber which is so extensively used where very high insulation is required. The reasons for this are its high cost, its mechanical limitations, and the fact that it deteriorates rapidly when exposed to light. Many insulating materials have made their appearance in recent years, yet there is very little data concerning them. This investigation was undertaken to determine the rate of deterioration of hard rubber and to make certain tests upon

other materials to see if their electrical properties permit them to replace hard rubber, at least for certain uses. Incidentally, many substances were tested which can be considered as hard rubber substitutes only in special cases.

The suitability of an insulating material for any given purpose will depend upon its mechanical properties fully as much as upon its electrical properties. It is not, however, the purpose of this paper to discuss the mechanical properties¹ of the materials considered.

There are several electrical properties of insulators between no two of which is there a known relationship. The most important of these are (1) the volume resistivity of the material, (2) the leakage over the surface, (3) the dielectric absorption, (4) the dielectric strength, and (5) the dielectric constant. All of these properties are functions of the temperature, and some may also be affected by other physical conditions, such as applied voltage, humidity, pressure, etc.

The relative importance of these properties depends upon the use to which the material is to be put. In high tension installations a knowledge of the dielectric strength is of the greatest importance, but even here information concerning the other properties may be useful. However, in many cases the surface leakage will tell much more than the dielectric strength as to the suitability of a material for a given class of work. For instance, the important properties of a material to be used for insulating the terminals of resistance coils are its volume resistivity and surface leakage, the latter being usually the more important. Another similar case is the insulation of the terminals of condensers, especially those of small capacity.

Fortunately in low voltage work the commercial demands upon insulators do not require that they shall possess any one of the properties enumerated above in an unusual degree. Hence, in most cases there is a considerable number of insulators which, from an electrical point of view, will satisfy the requirements. The choice will then turn on the mechanical qualities and cost. However, cases frequently arise where one or more of the electrical qualities are the first consideration, and in such cases it is

¹ Both the electrical and mechanical properties of insulators are now being investigated by the "Kommission für Isolierstoffe," a preliminary report by Dr. H. Passavant appearing in the *Elektrotech. Ze.*, 88 p. 450; 1912.

important to have reliable data available. A considerable amount of data concerning the dielectric constant and dielectric strength of insulating materials has been published, but even in this field much remains to be done. The absorption in dielectrics is only beginning to be carefully studied. The volume resistivity of dielectrics has been extensively studied, but it is often difficult to find reliable data upon materials in common use. The importance of surface leakage has long been appreciated, but it is only within a few years that careful measurements³ upon it have been made.

This paper presents results upon the volume resistivity and surface leakage of a number of insulating materials. The surface leakage was measured under varying conditions of temperature and humidity both before and after exposure to light. The volume resistivity was measured at different temperatures and the effect of absorbed moisture and of the magnitude and length of time of application of the voltage was studied. The aim has been to cover all the conditions that will normally be found in a physical laboratory.

II. METHODS

The methods employed may naturally be classed under two heads: (1) The methods of measuring the resistance; (2) Methods of preparing the specimen. Under the latter will fall the methods of maintaining the specimen under the desired conditions.

1. METHODS OF MEASURING THE RESISTANCE.

In measuring the resistance high accuracy was not required. An accuracy of 10 per cent was considered sufficient. As a large number of samples were measured, and each sample measured several times, it was necessary to arrange the apparatus so that it could be worked rapidly. Measurements were made from 10^4 ohms to 10^{17} ohms, the upper limit being fixed by the sensibility of the apparatus.

It was found impossible to measure such an extreme range of resistance in a single set up. Hence, two different methods were employed: (a) The galvanometer method; (b) the electrometer method.

³ The following are a few of the important references to this work: Mershon—High Voltage Measurements at Niagara, *Trans. A. I. E. E.*, 27, p. 845; 1908. Dietrich—On the Conductivity of Electric Insulators, *Diss. Göttingen*, 1909, and *Phys. Zs.*, 11, p. 187; 1910. Rebora—Experimental Researches on Insulators of Glass and Porcelain, *Atti dell'Associazione Elettrotecnica Ital.*, 14, p. 665; 1910. Passevanti—Loc. cit. Schroedinger—On the Conductivity of Electricity Over the Surface of Insulators in Humid Air. *Acad. Wiss. Wien, Sitz. Ber.*, 119, 2a, p. 1215; 1910.

(a) THE GALVANOMETER METHOD

The diagram of Fig. 1 shows the galvanometer method as arranged for measuring the volume resistivity of the specimen. The terminal F of the battery is connected to the mercury on which the specimen floats. The current flows through the specimen to the mercury contained in an open cylinder of known area which is connected to D. The megohm in series serves to protect the galvanometer and is usually negligible relative to the resistance of the specimen. To prevent the current which flows over the surface of the specimen from reaching D, a guard ring of mercury surrounds the inner cylinder, but is insulated from it. This guard ring is connected directly to the opposite terminal of the battery. In measuring a surface resistance or any resistance in which a guard ring is unnecessary the unknown resistance is connected directly between D and F.

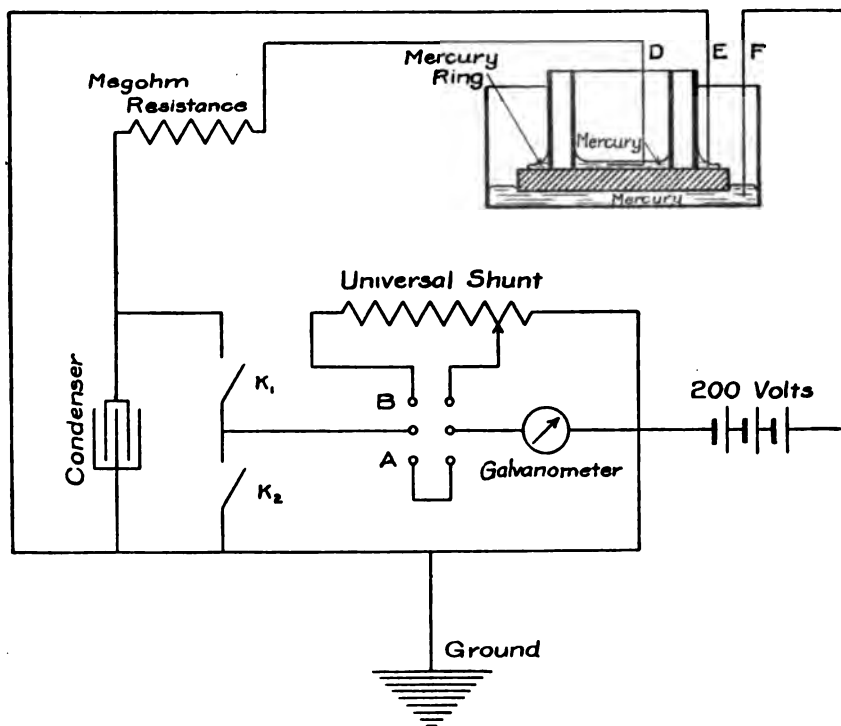


FIG. 1.—Connections for measuring volume resistivity by the galvanometer method

For supplying the voltage, trays of small storage cells are used. This battery and the other apparatus are placed on metal plates which are grounded. One terminal of the battery is also connected to the same ground. The key K_2 is for short circuiting the galvanometer, while the key K_1 closes the circuit through the galvanometer. When the double throw switch is in the direction B, the galvanometer is connected in parallel with a universal shunt. This can readily be adjusted so that 1, 1/10, 1/100, 1/1000, or 1/10000 of the total current passes through the galvanometer. The Sullivan galvanometer had a current sensitiveness of 2000 mm per microampere, with a scale distance of 2 meters. Using a battery of 200 volts, as was done in almost all cases, resistances from 10^4 to 11^{11} ohms can be measured to an accuracy of 10 per cent. When the double-throw switch is thrown to A, the galvanometer is connected directly in series with the specimen without the damping resistance which is contained in the universal shunt. If the current is so small that it does not produce an appreciable deflection upon closing the key K_1 , the key is opened so that the current flowing through the specimen will charge the condenser. At the end of a time t , the key K_1 is again closed and the charge which has accumulated is discharged through the galvanometer. From the ballistic constant of the galvanometer, the resistance of the specimen can be computed in the following manner.

If Q is the quantity of electricity upon the condenser of capacity C at a time t after opening K_1 , i the current flowing through the specimen and R its resistance, then since $Q = \int_0^t i dt$

$$E = Ri + \frac{1}{C} \int_0^t i dt.$$

The solution of this integral equation gives $i = \frac{E}{R} e^{-\frac{t}{RC}}$

and hence $Q = EC (1 - e^{-\frac{t}{RC}})$

Expanding the exponential

$$Q = \frac{Et}{R} \left(1 - \frac{t}{2RC} + \frac{t^2}{6R^2C^2} - \dots \right)$$

Hence, if $t/2RC$ is small relative to unity,

$$R = \frac{Et}{Q} = \frac{Et}{Kd}$$

where K is the ballistic constant of the galvanometer and d the deflection. This method of computing does not introduce an error of more than 1 or 2 per cent, which for our purpose is sufficiently accurate.

The condenser should have negligible leakage and absorption. This was secured by placing an air condenser, insulated by glass pillars, in a chamber dried with phosphorus pentoxide. The Sullivan galvanometer had a ballastic sensitiveness of 1400 mm per microcoulomb with a scale distance of 2 meters. By this method resistances from 10^{11} to 10^{16} ohms can be measured. It would appear that there should be no limit to the resistances that can be measured provided the time of leakage is sufficiently long. However, in practice it was found impracticable to use a time longer than five minutes, so that a resistance of more than 10^{16} ohms could not be measured by this method.

(b) THE ELECTROMETER METHOD

For measuring resistances higher than 10^{16} ohms a Dolezalek quadrant electrometer having a capacity of $130 \mu\mu\text{f.}$ was employed. By means of it resistances as high as 10^{17} ohms could be measured. The diagram of Fig. 2 shows the connections for measuring the surface resistivity. The lead to one pair of quadrants is entirely surrounded by an earthed shield, while the other pair of quadrants is connected to earth. The surface leakage is over the surface between the inner and outer cylinders which rest on the insulator.

To measure the volume resistivity of the specimen, the battery B is disconnected from the outer ring and connected to the mercury in which the specimen is floated (see Fig. 1). The outer ring is then connected to earth. The current which flows onto the inner quadrant must now flow through the specimen.

If the needle of the electrometer is maintained at a constant potential, the deflection of the needle will depend on the quantity of electricity on the inner quadrant. If the external electromotive force E is high relative to the counter electromotive force due to the charge on the quadrants, then the current through the insulator may be considered constant. In this case $R = \frac{E}{I} = \frac{Et}{Q} = \frac{Et}{Kd}$, where

E is the applied electromotive force, t the time necessary to produce a deflection d , and K is the quantity of electricity necessary to produce unit deflection. This is similar to the method using a ballistic galvanometer, but differs in that the quantity can be determined at any instant.

To determine the constant of the instrument, a sample whose resistance could be measured by both the galvanometer and electrometer methods was employed. To obtain a check upon this, two

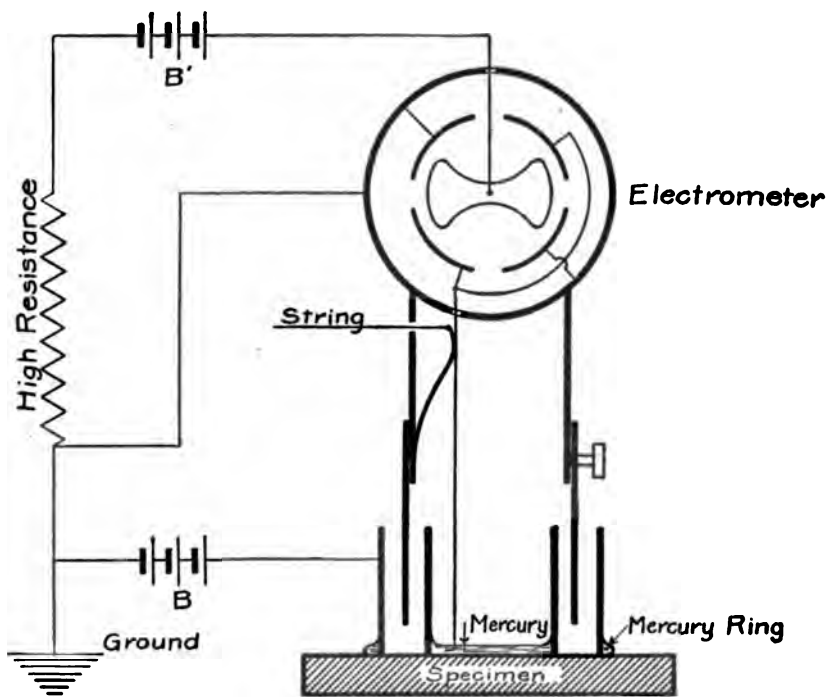


FIG. 2.—Connections for measuring surface resistivity by the electrometer method

other samples were chosen having resistance higher and lower, respectively, than the one indicated above. The lower resistance was measured first with the galvanometer method, and then with the electrometer method using a shunt of several thousandths of a microfarad to reduce the sensitivity of the electrometer. The sample of higher resistance was then measured using the electrometer both shunted and unshunted. The two methods of ob-

taining the constant K gave concordant results, the value being 6×10^{-10} coulombs for a deflection of a cm. at a scale distance of 1.3 meters with 100 volts on the needle.

2. METHODS OF PREPARING THE SPECIMEN

For measuring the surface leakage, the material was obtained, whenever possible, in plates 10 cm square by 1 cm thick. Metal strips 1 cm wide were clamped to this with their adjacent edges 1 cm apart, as shown in Fig. 3. The resistance was measured between strips A and strips B. The surface resistivity is assumed to be twenty times the resistance measured. (Surface resistivity

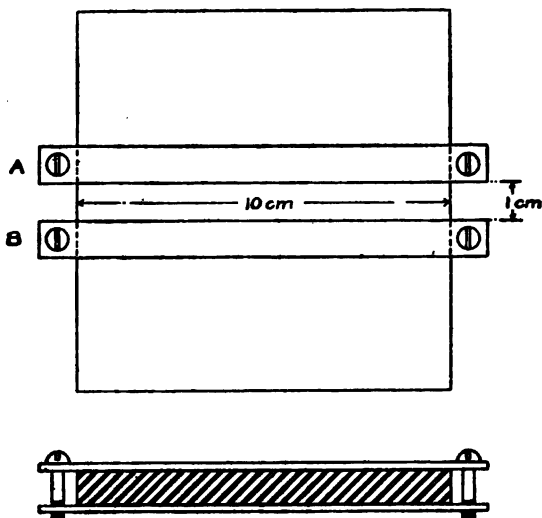


FIG. 3.—Specimen arranged to measure surface resistivity

is defined in Sec. IV below.) While this is not strictly true, since there is leakage over the edges as well as over the face of the specimen, yet the correction is too small to take account of in the present work. To insure good contact, tinfoil was wrapped around the metal strips and carefully pressed against the surface of the insulator along the inside edge of each strip.

In some cases tubes of the material were used. In such cases wires were tightly twisted around the tube at a distance of 1 cm apart and the resistance between these wires measured.

For determining the effect of temperature and humidity it was necessary to place the samples in a case, the temperature and

humidity of which could be maintained constant. The temperature was maintained constant by a vapor pressure thermostat. The humidity was regulated by placing in the case an open vessel containing a sulphuric acid solution of the proper strength to give the desired humidity. The curve of Fig. 4 was constructed from Regnault's data, and from it the correct strength of acid could readily be determined. For very low humidities phosphorous pentoxide was used in the place of sulphuric acid. It was found necessary to keep out of the case all large blocks of wood and other absorbing materials. The air was thoroughly stirred by an 8-inch

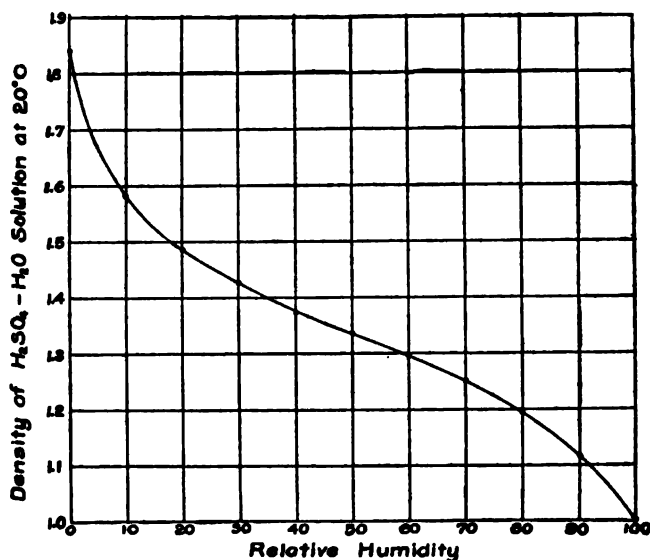


FIG. 4.—Curve showing the relationship between the density of a sulphuric acid solution and the relative humidity which will be maintained by it in an inclosure

fan, the driving motor being outside of the case. The leads to the specimens were brought out through blocks of paraffin on the top of the case. These were melted together, so that the case was sealed almost air-tight. A glass window permitted the reading of the temperature and humidity.

The humidity was measured by determining the temperature at which dew would form on a polished metal surface. The deposit of dew was usually obtained by circulating cold water through a metal tube, but for very low humidities it was found necessary

to use alcohol in the tube and cool it by adding carbon dioxide snow.

For measuring the volume resistivity, the material was floated on mercury and an amalgamated copper block surrounded by a guard ring placed on the upper side. It was hoped in this way to reduce contact and surface leakage errors to a minimum, but in some cases such errors were found to exist. Therefore, in the later work the copper block was replaced by a copper tube in which, after placing it upon the specimen, sufficient mercury was poured to cover the bottom. A ring of mercury was also made around the outside of the guard ring, so that all contacts were of mercury.

III. VOLUME RESISTIVITY

The volume resistivity of a material is defined as the resistance to the current flowing through the material between two opposite faces of a centimeter cube. The direct measurement consists in measuring the resistance between two opposite faces of a slab of the material, using electrodes of known area. To insure that the electrodes were in contact with the material, mercury electrodes were employed. To eliminate surface leakage from the measurements, a guard ring of mercury was used. The arrangement is seen in Fig. 1. As a check upon the results, two sets of electrodes whose areas were in the ratio of 3 to 1 were generally used. The values of the resistivity as determined from these two areas did not often vary by more than 10 per cent.

1. EFFECT OF HUMIDITY*

In certain cases results taken at different times did not agree satisfactorily. In seeking a cause for this, the question naturally arose as to whether the humidity of the air in which the sample had been kept before being measured could affect the volume resistivity. In order to test this, samples which had been maintained for some time in air of one humidity were surrounded by air of another humidity and maintained in this condition for several weeks. The volume resistivity was measured at frequent intervals during this time.

* Evershed (J. I. E. E., 52, p. 51; 1914) has published an elaborate investigation on the effect of moisture on volume resistivity, using very porous materials such as paper and cloth.

The results show that, in certain cases, the volume resistivity decreases with increasing humidity but that an equilibrium is reached only after a very long time. To illustrate this, several curves obtained from one series of experiments are given in Fig. 5. The samples were maintained at a high humidity (about 90 per cent) for more than a month prior to December 4, 1913, when the

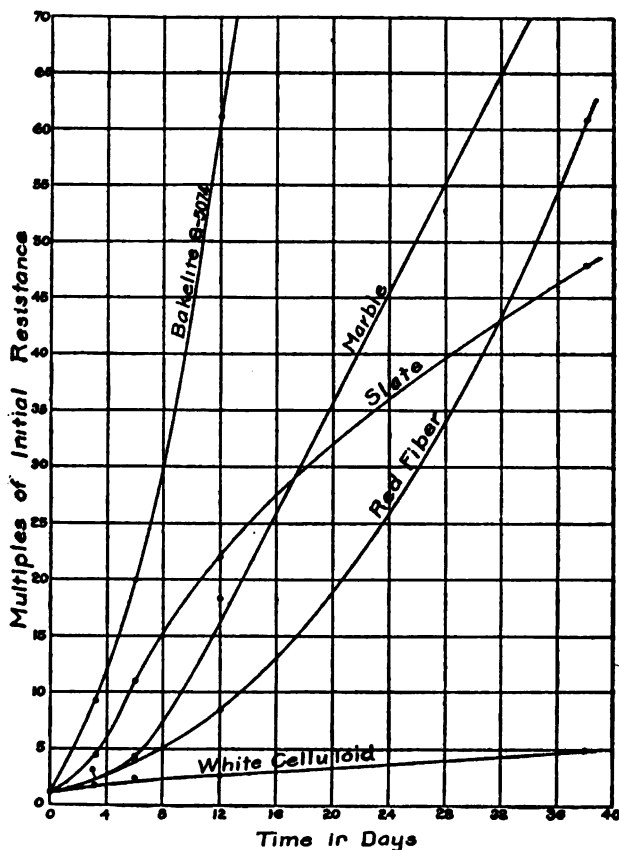


FIG. 5.—Increase in the volume resistivity of certain materials caused by a loss of absorbed moisture

humidity of the tank was decreased to 25 per cent and maintained at this humidity and a temperature of 25° C until January 12, 1914. Measurements were made at the times indicated in the figure. In many cases there was a progressive increase in the resistance and for most of these samples an equilibrium had not

been reached at the end of 40 days. Of the five curves given, celluloid shows the least change, while bakelite No. G5074 shows the largest. The celluloid has five times the resistance which it initially had, while the bakelite has over 300 times as much. This sample of bakelite contained talc as a filler. A more complete statement of its composition will be found in Table 4, page 399.

It is well known that marble, slate, and hard fiber absorb water in considerable quantities. The curves show that they lose this water very slowly. In the case of slate it is apparent that a definite value is being approached, but for some of the others no such statement can be made. The indefiniteness of the volume resistivity of materials which absorb water is very apparent. Where changes take place as slowly as in these cases it is not feasible to determine the change of volume resistivity with humidity.

A number of samples were measured besides those whose curves are given in Fig. 5. In some cases very interesting results were obtained. It is known that shellac absorbs moisture to an appreciable extent, yet no change of resistivity with humidity was observed. In the case of glass the results upon one sample indicate a slight change of resistivity with humidity, but it is too small to announce with certainty. Some of the molding compounds—electrose, gummon, and molded mica—showed no measurable change.

2. EFFECT OF VOLTAGE

Observations which have been made on the change of the volume resistivity of insulators with voltage show a wide variation in the results. Many observers have found that the resistance of certain insulators which they were studying did not depend on the voltage, while others have found that the resistance decreases as the voltage increases. It is to be expected that there will be a decrease in the resistance when the voltage is so high that breakdown is approaching, but in some cases it has been observed when very far removed from breakdown. The literature on this subject is so large, that no adequate review of it can be undertaken here. Mention will be made of only one article.

Evershed ⁴ has investigated certain porous materials such as paper and cotton cloth. For very low voltages, he finds that the resistance decreases rapidly with increasing voltage, becomes nearly stationary at higher values, and again drops rapidly at still higher values. In the region of low voltages, he finds that if the voltage is increased by a factor of 10 the resistance decreases by a factor of about 2.2. He has developed a theory for this change which depends upon the condensation of moisture in the pores of the material.

Measurements upon similar materials in this laboratory confirm his results. However, the materials used in this investigation are of such a different character that similar results are not to be expected. The results upon a number of materials are given in Table 1. It will be seen that only in one-third of the specimens is there any appreciable change in going from 50 to 500 volts, and of these the majority are known to be porous. In the case of opal glass there was an increase in resistance with increasing voltage and while this was confirmed by several measurements, no other material was found which gave a similar result.

TABLE 1
Table Showing Change of Volume Resistance with Voltage

Material	Thick- ness of specimen	Ratio of resistance at 50 volts to the resistance at 500 volts	Material	Thick- ness of specimen	Ratio of resistance at 50 volts to the resistance at 500 volts
	cm			cm	
Yellow electrose.....	1.27	1.0	Bakelite No. 150.....	0.97	1.0
Hemit.....	0.73	1.0	Bakelite No. 151.....	.98	1.0
Tegit.....	.78	1.0	Bakelite No. 190.....	.96	1.0
Gummon.....	.62	1.0	Bakelite No. 192.....	.99	1.1
Red fiber.....	1.27	1.0	Bakelite No. G5074.....	.95	1.9
Hard fiber.....	1.23	1.0	J-P Bakelite.....	.60	2.0
Redmonite.....	.13	1.0	Slate.....		1.1
Paraffined maple.....	2.3	1.0	Marble:		
Paraffined poplar.....	1.8	1.0	Pink Tennessee.....	2.25	1.4
Yellow condensite.....	1.32	1.0	Blue Vermont.....	2.3	2.0
Black condensite.....	1.28	1.0	Italian.....	2.2	2.5
Bakelite No. 140.....	.96	1.0	Opal glass.....	.17	.7
Bakelite No. 141.....	.99	1.0			

⁴ J. I. E. E., 52, p. 51; 1914.

No results are given for the very best insulators since, as will be shown later, the effect of dielectric absorption is so large that any possible change of resistance with voltage is entirely masked.

3. EFFECT OF TEMPERATURE

The variation of the volume resistivity of insulators with temperature has been the subject of many investigations. The majority of these have used a wide range of temperatures and have only estimated the change in resistivity corresponding to the ordinary fluctuation of room temperature by extrapolation from much higher temperatures.

A large number of the ordinary insulators were investigated by Dietrich⁵ between the temperatures of 20° and 200° C., though the measurements at temperatures below 50° C. were not very satisfactory. He found that the results could be approximately represented by the formula⁶

$$R_t = R_0 e^{\frac{-q}{273(273+t)}}$$

where R_t is the resistance at any temperature t , R_0 the resistance at zero centigrade and q a constant which depends upon the material. The values of q lie between 4000 and 25 000. For the range 20° to 30°, the smaller value of q corresponds to a decrease in the resistance of 50 per cent, while for the larger value of q , the resistance at 20° is 17 times as large as at 30°.

In Table 2 are given the values found in this laboratory. The range of temperature has been from 20° to 30° C. in every case. The substances used are sufficiently representative to indicate what may ordinarily be expected in this range.

⁵ Concerning the conductivity of electric insulators Diss. Göttingen, 1909. An abstract is to be found in *Phys. Zs.*, 11, p. 187; 1910.

⁶ From considerations of the electron theory, Koenigsberger & Reichenheim (*Phys. Zs.*, 7, p. 570; 1906) derived the formula

$$R_t = R_0(1 + \alpha t + \beta t^2) e^{\frac{-qt}{273(273+t)}}$$

for the change of resistivity with temperature for any body. The terms containing α and β are negligible in the case of insulators. The formula of Rausch & Hinrichsen (*Zs. für Elektrochemie* 14, p. 41; 1908) is equivalent to this modified formula. Most of the work which has been done to check these formulas has been at temperatures above 100° C.

TABLE 2

Table showing the Decrease of Volume Resistivity with Increasing Temperature

[ρ_{20} —Volume resistivity at 20° C; ρ_{30} —Volume resistivity at 30° C]

Sample	ρ_{20}	ρ_{20}/ρ_{30}	Sample	ρ_{20}	ρ_{20}/ρ_{30}
Sealing wax.....	1.9×10^{14}	0.9	German glass.....	2.0×10^{12}	2.5
Mica (India ruby, slightly spotted).....	1.0×10^{17}	1.0	Halowax.....	1.3×10^{12}	2.5
Insulate No. 2.....	8.4×10^{14}	1.0	Yellow electrose (D).....	3.3×10^{14}	2.6
Henalt (a).....	2.1×10^{14}	1.2	Bakelite No. G5074.....	2.3×10^{14}	2.6
G. E. No. 55A.....	1.3×10^{14}	1.2	Red fiber.....	7.8×10^{12}	2.6
Moulded mica.....	2.0×10^{14}	1.2	Bakelite No. L558.....	1.0×10^{14}	2.6
Mica (brown African clear).....	1.7×10^{14}	1.2	Mica (India ruby, stained).....	2.2×10^{12}	2.7
Henalt (b).....	5.7×10^{12}	1.4	Opal glass.....	5.0×10^{11}	2.8
Tagit.....	1.9×10^{12}	1.4	Yellow condensite.....	1.7×10^{12}	2.9
Gummen.....	3.4×10^{12}	1.4	Black condensite.....	4.8×10^{12}	2.9
Shellac.....	1.2×10^{14}	1.5	Tetrachloronaphthalene.....	1.7×10^{12}	2.9
Ivory.....	1.5×10^{12}	1.6	Glyptol.....	7.4×10^{14}	3.0
J-P Bakelite.....	1.2×10^{14}	1.6	Dielectrite.....	2.2×10^{12}	3.0
Unglazed porcelain.....	2.2×10^{14}	1.6	Hard fiber.....	1.0×10^{12}	3.2
Yellow stabilite.....	4.3×10^{12}	1.6	Plate glass.....	1.0×10^{12}	3.2
G. E. No. 40.....	6.7×10^{14}	1.6	German glass (special).....	5.0×10^{12}	3.5
White collinoid.....	1.4×10^{14}	1.8	Bakelite No. 4.....	3.3×10^{12}	3.6
Murdock No. 200.....	3.2×10^{14}	1.8	Bakelite No. 190.....	4.2×10^{12}	3.6
Murdock No. 201.....	5.2×10^{14}	1.8	Bakelite No. 150.....	1.9×10^{12}	3.6
Mica (clear).....	1.1×10^{17}	2.0	Paraffined maple.....	1.9×10^{12}	3.6
Parawax.....	2.6×10^{14}	2.0	Paraffined poplar.....	2.3×10^{12}	3.6
Redmonite No. 183, 1.....	4.7×10^{12}	2.0	Resin.....	1.7×10^{14}	3.6
Black electrose.....	6.0×10^{12}	2.0	Kavalier glass.....	2.0×10^{14}	4.5
Vulcabeston (a).....	8.4×10^{12}	2.3	Sulphur.....	3.9×10^{12}	4.9
Yellow electrose (L).....	4.7×10^{14}	2.3	G. E. No. 55R.....	5.9×10^{14}	5.1
Bakelite No. 140.....	7.5×10^{12}	2.4	Bakelite No. 5200 RGR.....	1.2×10^{11}	5.3
Bakelite micarta.....	2.7×10^{14}	2.4	Khotinsky cement.....	2.1×10^{14}	11.0
			Yellow beeswax.....	4.0×10^{14}	16.0

NOTE.—Values are for individual samples. For the volume resistivity of materials, as determined by measurements upon several samples, see Table 3.

4. EFFECT OF DIELECTRIC ABSORPTION

The system of two opposite electrodes separated by a dielectric such as that used in measuring the volume resistivity of insulators may also be considered as a condenser. Hence, at the instant of closing the circuit the current will be largely due to the displacement through the dielectric, but this will become negligible in a few thousandths of a second. Also as in the case of all condensers using solid dielectrics there will continue to flow for some time a

current which is absorbed by the dielectric. This absorption current decreases with the time, approximately following an exponential law, and may not become negligible for several hours.

This absorption current is superimposed upon the current due to conduction. If the conduction current is large relative to the maximum value of the absorption current, the apparent resistance (ratio of electromotive force to the total current) is independent of the length of time that the electromotive force is applied. But if the conduction current is small, the absorption current may, for a time after the application of the electromotive force, be larger than the conduction current. The resistance can then be obtained only by applying the electromotive force for a sufficiently long time to make the absorption current negligible.

While accurate data are not as yet available concerning the absorption current, it is possible to get some idea of its magnitude, and hence to estimate at what point the absorption becomes an important factor. Immediately after applying the electromotive force the absorption current may be relatively large, but it decreases rapidly so that at the end of one minute the quantity absorbed per second is usually between $1/100$ and $1/100\,000$ of the quantity which was displaced through the dielectric. If we assume that the dielectric constant is five, then the absorption current at the end of one minute in the case of a cubic centimeter of the material having electrodes on opposite faces to which is applied a potential difference of one volt lies between 0.5×10^{-14} and 0.5×10^{-17} ampere. In order that the conduction current shall be at least ten times as large as this, the resistivity must be less than 2×10^{13} ohms in the first case, and 2×10^{16} ohms in the second case.

Hence in those cases where the volume resistivity is less than about 10^{13} ohms, the absorption current gives no error greater than 10 per cent, provided the resistance is measured at the end of a minute. However, if the resistivity is above 10^{13} ohms, measurements must be made with different time intervals in order to determine when the absorption current becomes negligible. If the resistivity is greater than 10^{16} ohms, the absorption current at the end of one minute will probably equal the conduction current and may be much larger. In such cases, it is necessary

to apply the voltage for a much longer time before the true conduction current can be obtained.

In Fig. 6 are curves showing the change of the apparent resistivity with time for two insulators having a resistivity greater than 10^{17} ohm-cms. In the case of hard rubber it will be seen that even at the end of half an hour the absorption current is more than ten times the conduction current. Even at the end of 18 hours we are not certain that the absorption current is negligible. For fused quartz the curve indicates that the change in the apparent resistivity continues for a long time. At the end of an hour the resistivity was so high as to be just measurable. At the end of 18 hours the resistivity was too high to measure, certainly above 5×10^{18} .

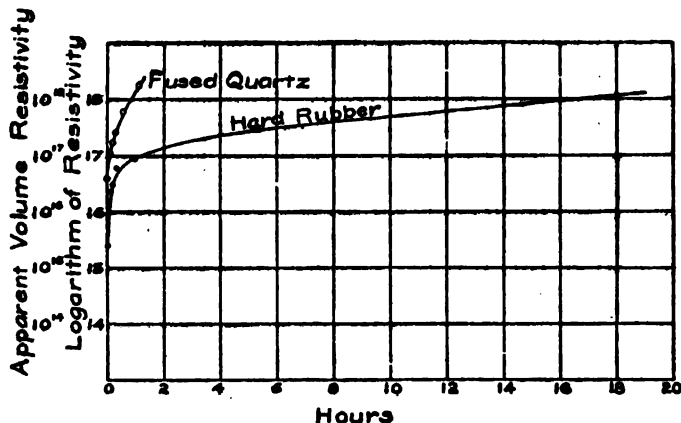


FIG. 6.—Effect of dielectric absorption upon the apparent resistivity

In Fig. 7 are given curves of the change of the apparent resistivity with time for a material at two different temperatures. The shape of the curves is somewhat different, showing that temperature modifies the absorption curves. At 30° the resistance had reached its maximum in about two hours, while at 20° the curve had an upward tendency at the end of seven hours.

5. VALUES OF THE VOLUME RESISTIVITY

The values of the volume resistivity of a large number of insulators arranged in order of their resistivities are given in Table 3. While measurements were made at various times during the course

of this investigation, yet the final measurements were made in March, April, and May, 1914. The specimens had been kept in the laboratory during the winter, and as the humidity of heated rooms is always low, the amount of moisture in those materials which absorb water was as low as will normally be found.

The determinations were made at room temperature, 22° C. Except in the case of some of the insulators having very high resistivity, the voltage was applied for a sufficiently long time to make the absorption current negligible. As time did not permit the determination of the resistivity for all materials, the apparent resistivity after the voltage has been applied for 15 minutes is given in certain cases. These are indicated by an asterisk. Very

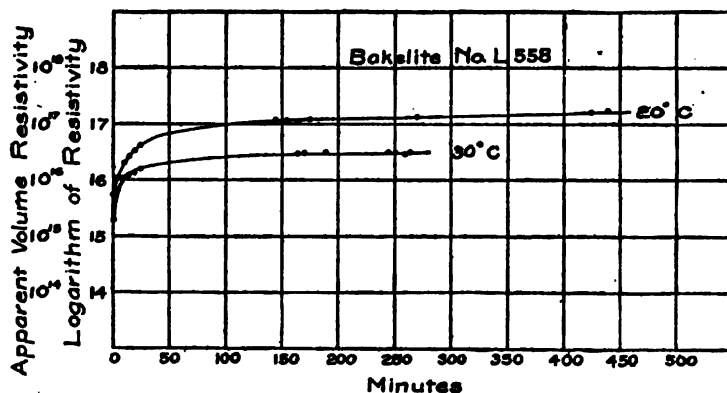


FIG. 7.—Effect of dielectric absorption upon the apparent resistivity

few of the materials are so uniform that two samples will give values of the resistivity as close as 10 per cent, while a factor of 10 or even more is not infrequent. Hence, it did not seem desirable to give more than one significant figure in the results, though in the measurements upon individual samples two significant figures were obtained whenever possible.

In Table 8 (appendix) the values of the resistivity are repeated, but the materials are arranged in alphabetical order. In addition are given values as obtained by other observers. This comparison may be of use in showing the variation that may be obtained with different samples, different conditions, and different methods of measurement.

TABLE 3

Volume Resistivity of Solid Dielectrics

[Materials arranged in order of decreasing resistivity]

Material	Resistivity	Material	Resistivity
	<i>Ohm-centimeters</i>		<i>Ohm-centimeters</i>
Special paraffin.....	Over 5000×10 ¹⁴	German glass.....	50×10 ¹³
Carsein.....	Over 5000×10 ¹³	Paraffined mahogany.....	40×10 ¹³
Fused quartz.....	Over 5000×10 ¹⁴	Stabalite.....	30×10 ¹³
Hard rubber.....	1000×10 ¹³	Plate glass.....	20×10 ¹³
Clear mica.....	200×10 ¹³	Hallowax No. 1001.....	20×10 ¹³
* Sulphur.....	100×10 ¹³	Dielectrite.....	5×10 ¹³
* Amberite.....	50×10 ¹³	Bakelite No. 5199 RGRB.....	5×10 ¹³
* Resin.....	50×10 ¹³	Bakelite No. 150.....	4×10 ¹³
* Mica (India ruby slightly stained).....	50×10 ¹³	Gummen.....	3×10 ¹³
G. E. No. 55 R.....	40×10 ¹³	Tegit.....	2×10 ¹³
Hallowax No. 5055 B.....	20×10 ¹³	Opal glass.....	1×10 ¹³
Bakelite No. L 558.....	20×10 ¹³	Paraffined poplar.....	500×10 ⁹
* Electroose No. 8.....	20×10 ¹³	Bakelite No. G 5200 RGR.....	400×10 ⁹
* Parowax (paraffin).....	10×10 ¹³	Bakelite No. 1.....	200×10 ⁹
Glyptol.....	10×10 ¹³	Bakelite No. 190.....	100×10 ⁹
* Shellac.....	10×10 ¹³	Italian marble.....	100×10 ⁹
Kavaller glass.....	8×10 ¹³	Bakelite micarta.....	50×10 ⁹
* Insulate No. 2.....	8×10 ¹³	Bakelite No. G 5074.....	40×10 ⁹
* Sealing wax.....	8×10 ¹³	Black condensite.....	40×10 ⁹
* Yellow electroose.....	5×10 ¹³	Yellow condensite.....	40×10 ⁹
* Duranoid.....	3×10 ¹³	Paraffined maple.....	30×10 ⁹
* Murdock No. 100.....	3×10 ¹³	White celluloid.....	20×10 ⁹
* Yellow beeswax.....	2×10 ¹³	J-P Bakelite.....	20×10 ⁹
Khetinsky cement.....	2×10 ¹³	Hard fiber.....	20×10 ⁹
Mica (brown African clear).....	2×10 ¹³	Black galalith.....	20×10 ⁹
* G. E. No. 40.....	1×10 ¹³	Lavite.....	20×10 ⁹
* G. E. No. 55 A.....	1×10 ¹³	White galalith.....	10×10 ⁹
* Moulded mica.....	1×10 ¹³	Hemlt.....	10×10 ⁹
Unglazed porcelain.....	300×10 ¹²	Red fiber.....	5×10 ⁹
Redmenite No. 157,4.....	200×10 ¹²	Pink Tennessee marble.....	5×10 ⁹
Black electroose.....	100×10 ¹²	Blue Vermont marble.....	1×10 ⁹
Tetrachloronaphthalene.....	50×10 ¹²	Ivory.....	200×10 ⁹
Mica (India ruby stained).....	50×10 ¹²	Slate.....	100×10 ⁹
		Bakelite No. 140.....	20×10 ⁹

* Apparent resistivity taken after the voltage had been applied for 15 minutes.

In making, tabulating, and interpreting the thousands of observations here presented, the greatest care has been exercised. At least two determinations have been made on each material, possible sources of error have been carefully considered, and, whenever feasible, two entirely different methods have been employed

with each sample. Also the results obtained have been compared as far as possible with those of other observers. It is our belief that the errors which finally remain are comparatively few.

IV. SURFACE LEAKAGE

The current which flows between two conductors, maintained at different potentials and insulated from each other by a solid material, is made up of two parts—that which flows through the insulator proper, and that which flows through a film of moisture or other conducting material on the surface of the insulator. The relative importance of these will depend on the resistance of the two paths. Since water, even if very pure, conducts much better than the ordinary solid insulators, a very thin film of water may have much less resistance than the insulator.

Before discussing these further, some definitions are desirable. The volume resistivity, ρ , of a material has already been defined as the resistance between two opposite faces of a centimeter cube. From the relationship between the size and resistance of a specimen it follows that

$$R = \frac{\rho l}{A} \text{ or } \rho = \frac{RA}{l}$$

where R is the resistance of a cylinder of cross section A and length l . By analogy we shall define the surface resistivity as the resistance between two opposite edges of a surface film which is one centimeter square. If the film is uniform over a surface

$$\sigma = \frac{R'b}{l}$$

where σ is the surface resistivity and R' the resistance of a rectangle of the film of length l and breadth b . If the thickness of the film is t , the volume resistivity of the film will be

$$\rho' = \frac{R'b t}{l} = \sigma t.$$

or $\sigma = \rho'/t$.

Since σ , the surface resistivity, depends upon the thickness of the film, it is not a property of the material of the film, and the term "resistivity," which is generally used to express the property of a material, can not strictly be applied. However, since both the thickness t and the volume resistivity ρ' of the surface film depend, under any given conditions, upon the material on which it is deposited, surface resistivity may be considered as a property of the material on which the film is deposited. Thus we will speak of the surface resistivity of glass, hard rubber, etc., though these materials only serve for condensing the moisture and do not carry any of the current.

It is quite impossible to devise a means for measuring the resistance of the surface film by itself, since some of the current will always flow through the insulator on which the film is deposited. However, by knowing the volume resistivity, a correction can be applied to the measured resistance to give the surface resistance. In only a few cases is this correction appreciable. A discussion of this correction is given on page 411, et seq.

It is sometimes convenient to have a term to express the total resistance between two conductors insulated by a solid dielectric. We shall call this the leakage resistance. We shall define the leakage resistivity as the resistance between two conductors, each 1 cm square, when they are placed 1 cm apart on an insulator 1 cm thick. While the leakage resistivity will in all cases be less than the surface resistivity, yet the difference between the two will usually be far less than the errors of measurement.

Since our measurements show that the surface film is largely moisture condensed from the surrounding atmosphere, the atmospheric humidity will largely determine the surface resistivity of a material. However, it is to be expected that the temperature of the specimen will be of some influence. Also since chemical changes are often produced by exposure to light, the surface resistivity of a material may be affected by such an exposure.

It might be expected that the applied voltage would affect the surface resistance, but, though a wide range of voltage was used in some cases, no change in resistance was ever observed. At high humidities the resistance frequently changed by as much as

a factor of 10 in the first minute after closing the key—increasing with some samples, decreasing with others. No cause for this behavior has been found. The value at the end of one minute has been taken as the correct value.

1. EFFECT OF HUMIDITY

In order to determine the effect of humidity upon the surface resistance of a material one or more samples were placed in the case already described, and their resistance measured at different humidities. While the procedure varied somewhat as the work progressed or as occasion demanded, the following method is the one usually employed.

A number of samples (50 was the maximum) were placed in the case and their leads brought out through the paraffin top. The thermostat was adjusted to maintain the temperature at about 25° in winter and 29° in summer. About 500 cc of sulphuric acid solution of the proper density to give the desired humidity was placed in a crystallizing dish in the bottom of the case and the case carefully sealed with paraffin. Measurements of the insulation resistance were made on the following day, after the samples had been kept in air at a given humidity for 18 or 20 hours. The case was then opened, the acid replaced by some of a different density, and the cycle repeated. This was continued until sufficient observations had been made.

The acid solutions were so chosen as to give relative humidities of 25, 50, 70, 85, and 95 per cent. In one case phosphorous pentoxide was used, giving a relative humidity of less than 0.1 per cent. In all cases the resistance was first measured at 25 per cent humidity. The usual procedure was then to increase the humidity by the steps indicated above until 95 per cent was reached, when the humidity was again lowered to 25 per cent.

After computing and tabulating the results, a curve was plotted for each sample showing its change of surface resistivity with the humidity. Nearly two hundred such curves have been plotted. From these, the curves given in Figs. 10 to 24 were selected. They cover practically all of the materials investigated, and were chosen as being representative of these materials.

Before discussing these curves, it will be desirable to consider the length of time necessary for the surface resistance of a substance to become stationary after a change of humidity of the surrounding air. In Fig. 8 is a curve showing the time rate of change of surface resistance of clean hard rubber when the humidity is increased from 50 per cent to 93 per cent. In this figure it should be noticed that the ordinates are the logarithms of the resistivities. It will

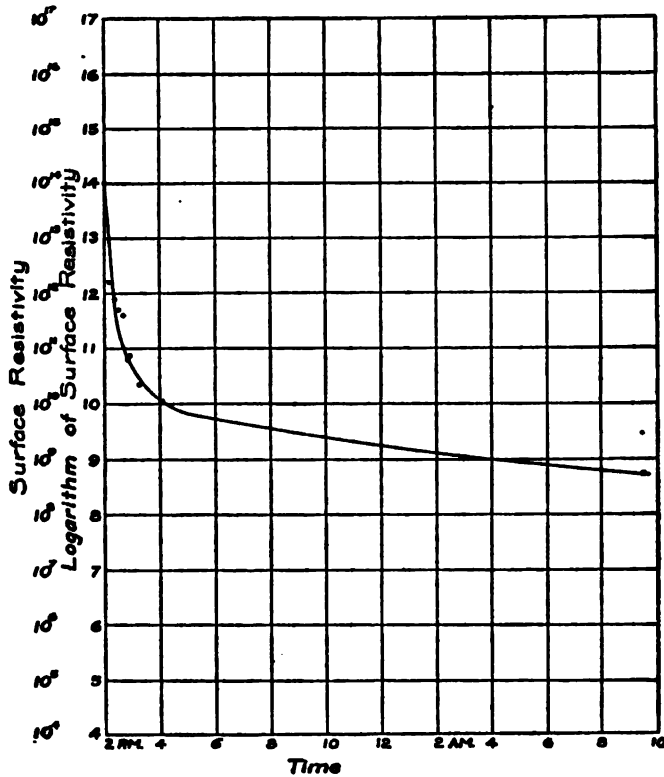


FIG. 8.—Curve showing the change in surface resistance with time of a piece of hard rubber when the humidity is increased from 50 to 93 per cent

be seen that the resistance changes rapidly for the first two or three hours, when the change becomes slower and is approximately exponential, as is shown by the fact that the curve is nearly a straight line when plotted as indicated above. While the change is comparatively slow after two or three hours, yet a steady state has not been reached at the end of 19 hours.

The change of resistance for three materials over longer periods of time is shown in Fig. 9. The scale in this case is different than in the preceding case, the ordinates being multiples of the initial resistance. The samples had been in air of 95 per cent humidity, then the humidity was lowered to 29 per cent. After remaining at this humidity for 48 hours, the initial reading was taken. The hard rubber which had deteriorated on account of exposure to

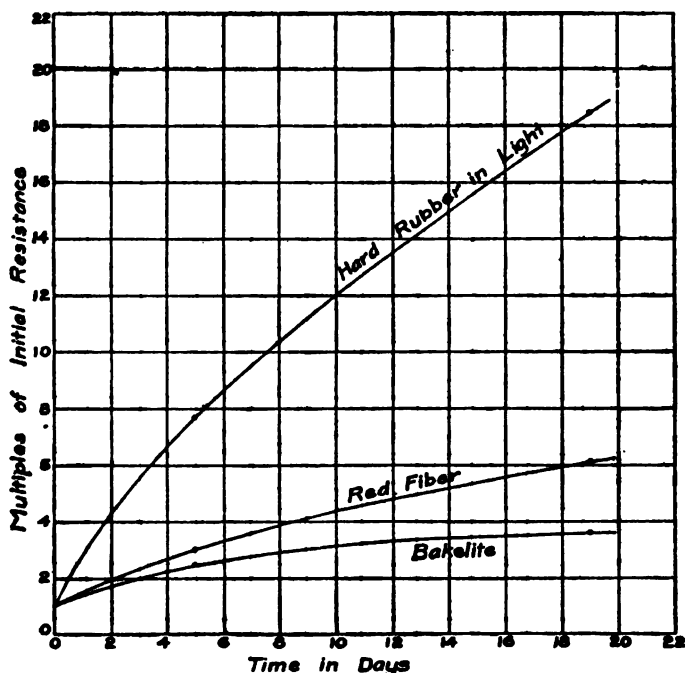


FIG. 9.—Curves showing the increase of surface resistance of specimens which had been in air at 95 per cent humidity and were then placed in air at 29 per cent humidity. The first readings were not taken until the specimen had been at the lower humidity for 48 hours

sunlight showed a very marked increase in the resistance and the maximum had not been reached at the end of 19 days. The other curves were selected as representing the change which takes place, when most insulating materials are subjected to a change in the humidity of the surrounding air. They show that precise results are of little value in the practical use of insulators.

Except in a few cases where it was desired to show the effect of cleaning, the samples were cleaned in the same manner and to the same extent as would be done in practical work; i. e., they were wiped with a cloth or dusted with a brush. The effect of traces of materials left on the surface will be discussed later.

All of the curves of surface resistivity given in Figs. 10 to 24 are plotted on the same scale, so that they can be readily compared. In order to make this possible, the logarithm of the surface resistivity is plotted as ordinate, so that the actual values of the surface resistivity progress by powers of 10. In this manner very large changes of resistance can be shown on one sheet. The abscissa is the per cent of relative humidity.

In order that the reader may judge for each sample concerning the lag of the surface resistivity after a change in the humidity of the surrounding air, those values which were taken with increasing humidity are indicated upon the curves by open circles, while those values which were taken with decreasing humidity are indicated by solid circles.

To economize space and to facilitate comparison of one curve with another it has been necessary to place several curves on one sheet. Where uncertainty might exist as to the curve to which a given point belongs, a fine line is drawn to connect the point with the curve.

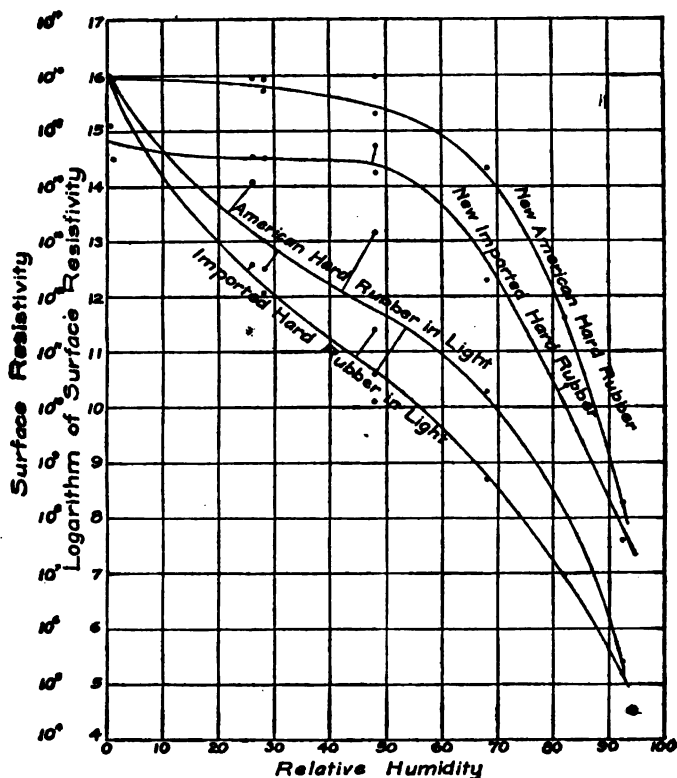


FIG. 10.—Change of surface resistivity with humidity of samples of hard rubber before and after exposure to sunlight

In Fig. 10 are given curves of four samples of hard rubber. Two had been protected from the action of the light, while two had been exposed to strong sunlight for several months. It will be noticed that between 0 and 50 per cent humidity the new rubber changes but little, while above that the changes are very pronounced. The surface resistivity is one *million* times as large at 50 per cent humidity as at 90 per cent. With the rubber which had been exposed to the light the changes in resistance continue until the lowest humidity is reached. The resistance of these specimens at very low humidity is 10^{11} times or one hundred billion times as great as is the resistance at 95 per cent humidity. It will be seen that very slight changes of the humidity will affect the insulation in a very marked manner.

Other samples of hard rubber have been tested, and those given may be taken as representative of the best grades of hard rubber. Of the two kinds whose curves are given, the imported rubber has a finer texture, and can be worked and polished better than the American rubber. However, all the tests upon the insulation show that the American rubber is the better insulator. This shows how difficult it is to connect the insulating properties with the mechanical properties.

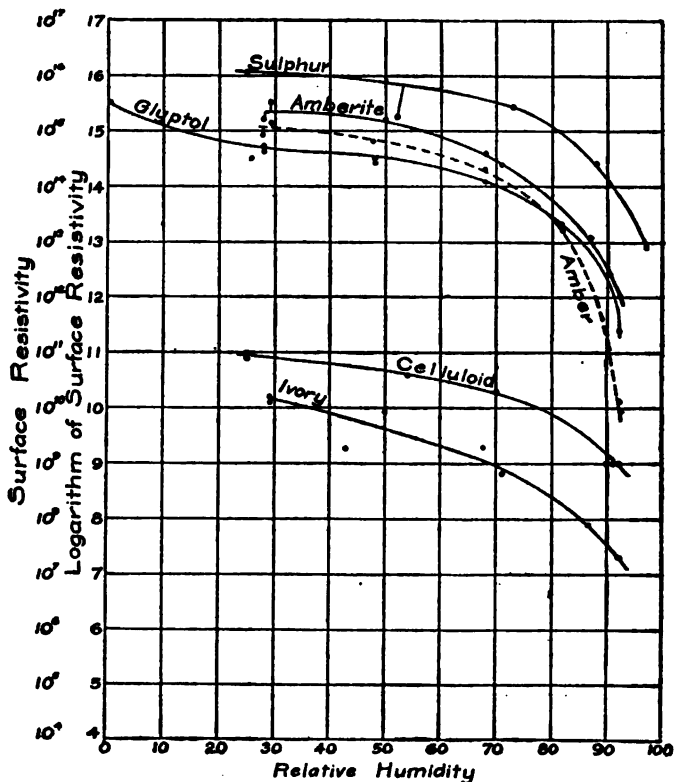


FIG. 11.—Change of surface resistivity with humidity of sulphur, ivory, and amber-like materials

Three of the curves given in Fig. 11 are for amber and amber-like materials. The sample of amber was a piece of clear native amber, the surface of which had been carefully polished. This is one of the few cases where only a single sample was measured. The amberite was a sample of the material which is made by compressing scrap amber. This material under the name of amberite or ambroid is now extensively used and it is apparent that so far as surface leakage is concerned it is the equal of native amber. In working with this material it was found that the specimen must be well cleaned to get the best results. Apparently handling with the fingers leaves a deposit of various deliquescent salts which condense moisture and lower the conductivity at the higher humidities. The glyptol is an artificial resin furnished by the research department of the General Electric Co. It resembles amber.

Three different samples of sulphur were tested. They showed wide variations. The curve which is given lay between those of the other samples. Threlfall states that sulphur heated just to its melting point and then cooled has better insulating properties than that which has been heated to a higher temperature before cooling. The sample of celluloid was a piece of clear celluloid. Several samples were tested having various amounts of coloring matter and filler, but the surface resistivity was substantially the same for all. Ivory can not be considered as a material having high insulating properties. A substitute, white galalith, is somewhat better. (See Fig. 22.)

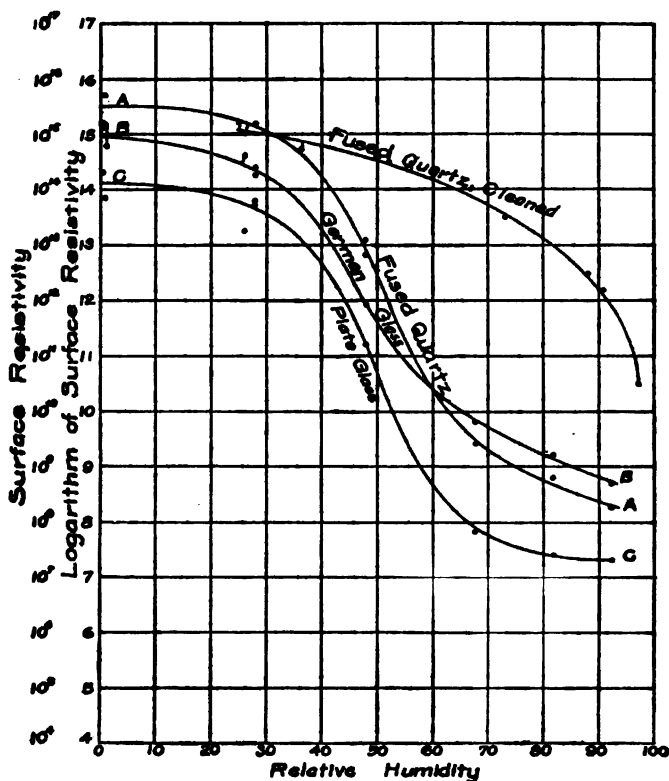


FIG. 12.—Change of surface resistivity with humidity of glass and quartz

In Fig. 12 the behavior of fused quartz and certain kinds of ordinary glass is shown. Several samples of quartz were tested, but the two curves given were for the same sample. The sample from which the curve marked "fused quartz" was obtained was cleaned in the same manner as other samples, but no special care was taken. It was carefully cleaned in strong chromic acid, washed in distilled water, and dried before obtaining the curve marked "fused quartz, cleaned." The surface was thus well freed from foreign substances. At low humidities there was no difference in the two specimens. At higher humidities there is a large difference, amounting to as much as a factor of ten thousand. This may be due to the lack of condensation of moisture on the cleaned specimen or to the fact that the water which is condensed has a lower conductivity. Doubtless both of these causes play a part.

The statement is sometimes made that the method of manufacture of fused quartz very decidedly affects the insulating properties of the product. This has not been substantiated by the results obtained in the course of this investigation. A piece of old quartz tubing made by Heraeus in 1904 was measured at the same time and under the same conditions as the sample marked "quartz, cleaned." The results were practically identical. Another sample of inferior manufacture gave, under the same conditions, the same results as given by the curve marked "fused quartz."

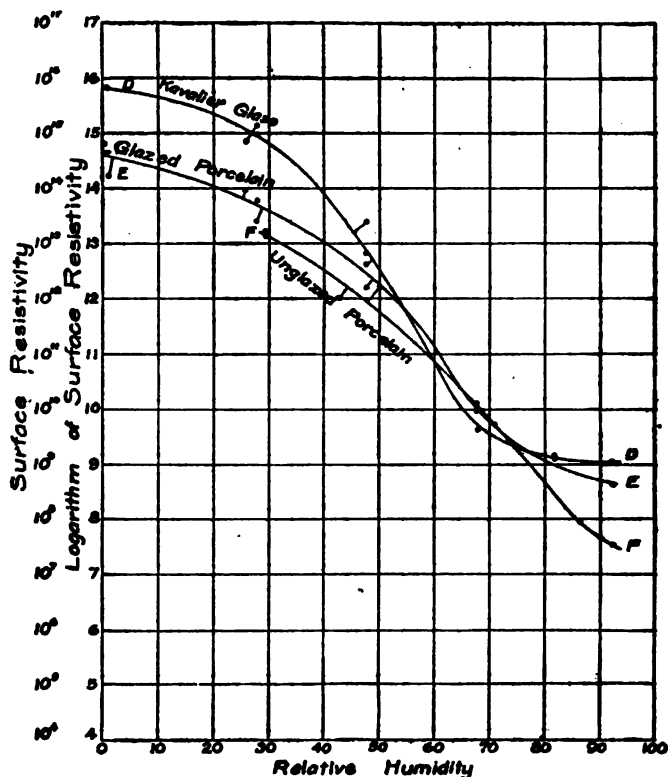


FIG. 13.—Change of surface resistivity with humidity of glass and porcelain

The curves for three kinds of glass are given in Figs. 12 and 13. The Kavalier glass is a very hard combustion tubing having a large potassium and calcium content and a small amount of sodium. The German glass is a soft glass tubing such as is usually used in glass blowing. The plate glass was a piece from a plate-glass window. It will be noticed that the curves fall very sharply at about 30 per cent humidity, and that above 70 per cent humidity the change is not so marked. These samples were tested twice with the results as given. Later they were cleaned with chromic acid in the manner described for quartz and the resistances measured a third time. While the results did not show such marked changes as in the case of quartz, they were all in the same direction. Also the effect was most pronounced on the hard Kavalier glass and least so on the plate glass. It is known that the Kavalier glass is less soluble⁷ than the other forms. Hence it is quite probable that the difference may largely be due to the difference in the conductivity of the water solution on the surface.

In Fig. 13 are also given curves for glazed and unglazed porcelain. The glazed porcelain was the base of a small porcelain switch, while the unglazed was a plate such as is used in chemical work.

⁷ Hovestadt: Jena glass, p. 333.

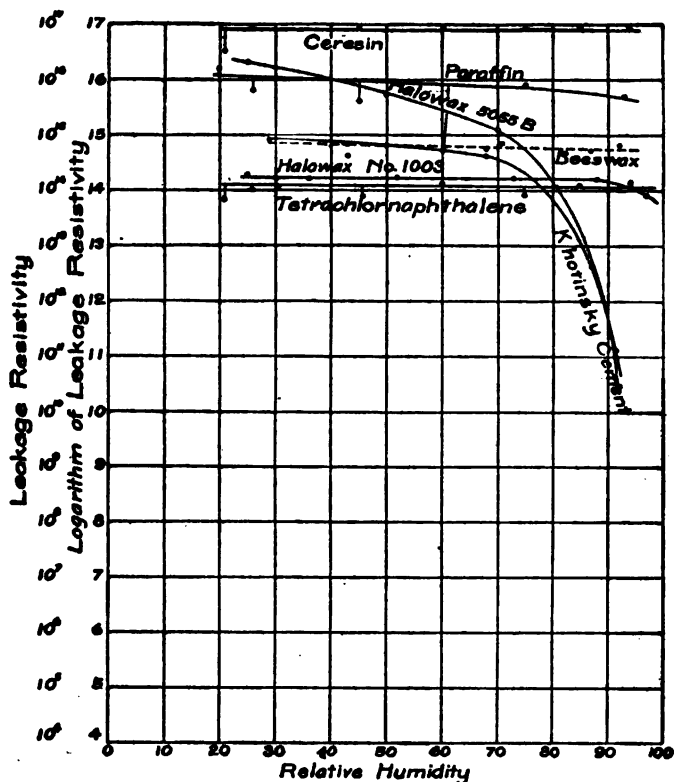


FIG. 14.—Change of leakage resistivity with humidity of waxes

In Fig. 14 are given curves for various waxy materials. It has been found impracticable to determine the surface resistivity of the most of these materials, so the results are given in terms of the leakage resistivity. Ceresin is refined from the mineral ozokerite. It somewhat resembles paraffin, but has a higher melting point (69°). An attempt was made to measure the leakage resistance of a sample at several humidities by the galvanometer method using a distance of 1 mm between the plates. It was impossible to obtain a readable deflection, but it is certain the values are above those given in the curve. With the electrometer method the surface resistivity was still too high to measure, certainly above 10^{16} ohms. A special paraffin having a melting point of 58° C. also gave results too high to measure by any method at our disposal. A commercial form of paraffin known as parowax (melting point 52°) gave the results shown in the curve. Measurements by the electrometer method gave a satisfactory check on these results.

The curve for beeswax was obtained from a sample of the yellow, unrefined material. White beeswax gave results which are almost identical. For these materials the surface must be fresh. They deteriorate quite rapidly when exposed to light and moisture.

The sample of tetrachloronaphthalene was furnished by Dr. Baekeland. It is doubtless a mixture of several isomers and may contain other chlorinated naphthalenes. It

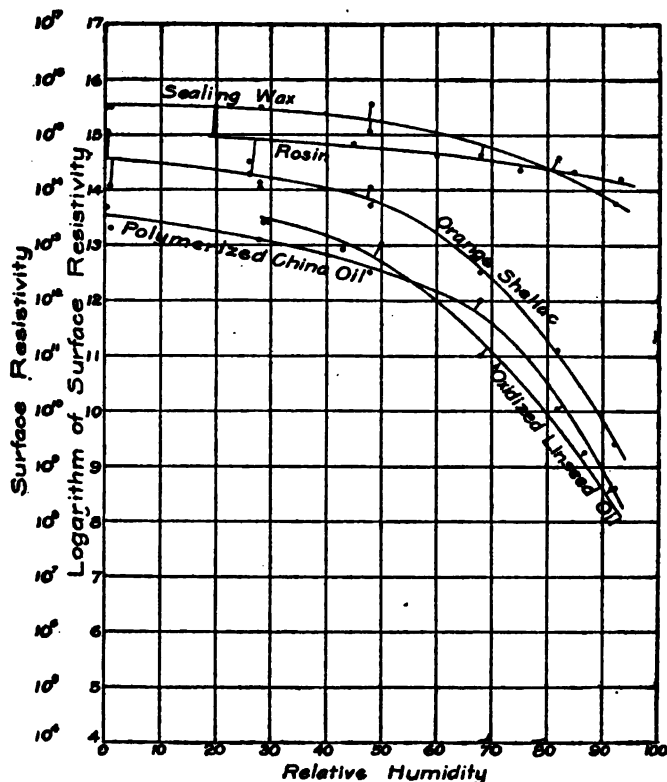


FIG. 15.—Change of surface resistivity with humidity of varnish materials

is about the consistency and color of yellow beeswax and has a very characteristic odor. The samples of "halowax" were furnished by the Condensite Co. of America. They are chlorinated naphthalenes. The sample No. 1003 is largely tetrachloronaphthalene. It is of a gray color, but in other respects has much the same properties, including odor, as the sample furnished by Dr. Baekeland. The sample 5055B is a higher chlorinated naphthalene, being largely hexachloronaphthalene.

The Khotinsky cement was flowed on a glass plate. The thickness was such that no appreciable part of the current flowed through the glass.

These waxy materials show the least change with humidity of any of the substances tested. This is doubtless due to the fact that the water does not wet the surface, hence instead of spreading over the surface is collected in minute drops.

In Fig. 15 are materials used in making varnish. The rosin is common rosin or colophony. It was melted and cast into a thick cake. The shellac, China oil, and linseed oil were applied to glass plates, several coats being used to obtain a sufficient thickness. The test upon a sample of white shellac gave results somewhat lower than for orange shellac. This was doubtless accounted for by the fact that the white shellac was not as thoroughly dried as the orange shellac.

The sealing wax was a stick of "treasury" wax. It consists largely of rosin, shellac, and coloring matter. It is of interest that the curve follows rosin more closely than shellac.

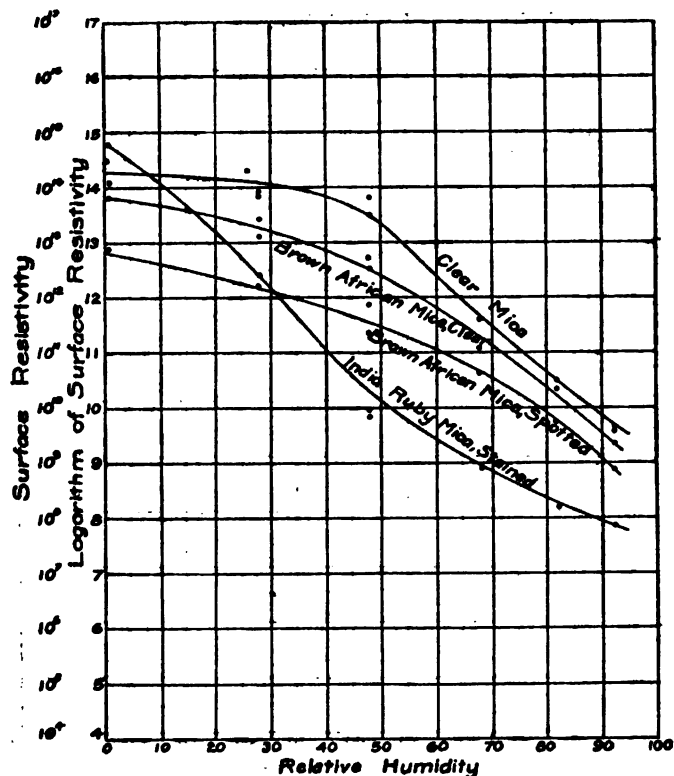


FIG. 16.—Change of surface resistivity with humidity of micas

In Fig. 16 are given the results upon samples of mica. The clear mica was entirely colorless. It was taken from a mica condenser. The surface was cleaned with gasoline, but it was not subjected to any treatment which would remove the last traces of paraffin and grease. Other samples were furnished by Meirowsky Bros., of New York, and the designations are those given by them. These designations indicate the color and source of the sample.

Another sample of India ruby mica was tested, which gave a curve nearly coinciding with the brown African mica, clear. These results are mainly interesting on account of the variability which is found in this material. It is evident that it would require an extended investigation to determine the relative merits of the different varieties of mica.

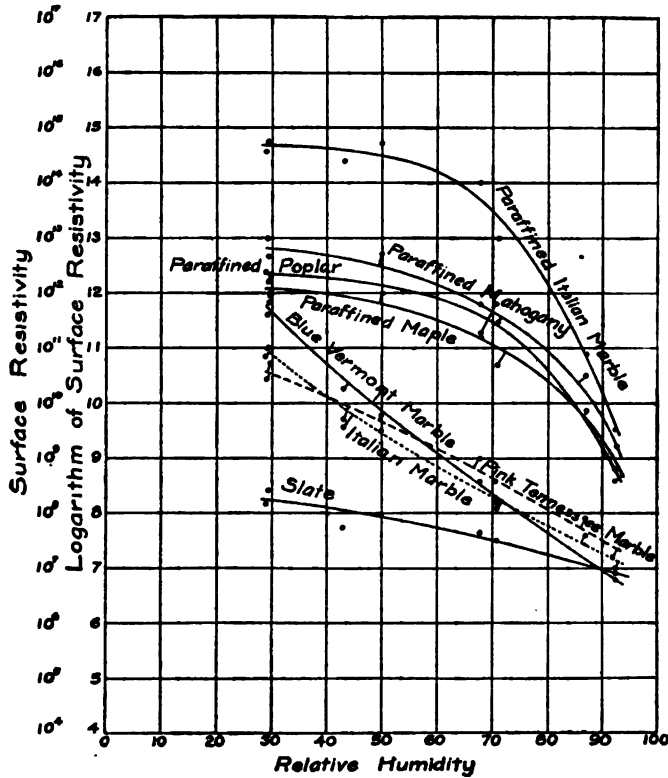


FIG. 17.—Change of surface resistivity with humidity of marble and paraffined woods

In Fig. 17 are grouped the curves of some of the poorer insulators, together with some curves showing the effect of impregnating them with paraffin. The slate was taken from the base of a switch and its origin is not known. The source of the marbles is stated on the curves. All were free from metallic veins, and were the equal of any that are used in switchboard construction. It appears that the coloring material in the Vermont and Tennessee marbles have very little effect on the surface leakage.

The marble and the different varieties of wood were impregnated with paraffin by keeping them in molten paraffin until no more air bubbles were given off. After cooling, the wood was planed and the marble sandpapered so that the resistance was measured over a surface of wood or marble with paraffin filling the pores and not over a layer of paraffin on the surface. The woods of more open grain such as mahogany and poplar show a somewhat higher insulation than the closer grained maple.

The paraffined marble shows the considerable increase in the insulation that may be obtained by impregnating with paraffin. The surface does not present as clear and pleasing appearance as before paraffining, and it accumulates dust more readily. The marked decrease of the resistance with increasing humidity is not readily explained. One would expect that it would behave more like paraffin which shows little change.

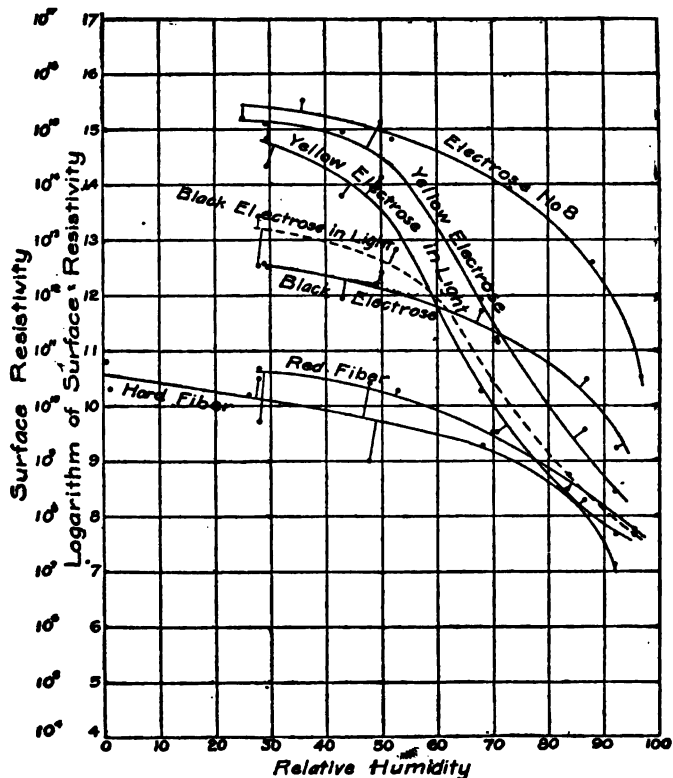


FIG. 18.—Change of surface resistivity with humidity of electrose and fiber

Beginning with Fig. 18 are given the results upon a number of materials which are manufactured under trade names. There are many materials in this class upon which results are not given, but the aim has been to include the most of the representative ones. For example, there are many firms making various bakelite compositions, many of them being sold under names which do not suggest their composition. Yet the values given under bakelite cover sufficiently well these materials.

The samples given in Fig. 18 are various varieties of electrose, together with red fiber and hard fiber. Hard fiber is made by treating a soft cotton paper with chloride of zinc. This reduces the paper to a jelly. The excess of zinc chloride is dissolved in water, after which the material is dried, pressed, and rolled.

The electrose samples were obtained from the Electrose Manufacturing Co., of Brooklyn. Two samples of two different kinds (black and yellow) were obtained several years ago. One sample of each kind was exposed to the light, while the other sample was kept in the dark. The results after exposing for three years are given in the curves. It will be noted that at low humidities the resistance of the sample of black electrose is higher after exposure to the light than before. This is doubtless due to the formation of fine cracks on the surface, which increase the leakage path at low humidities, but which are bridged by small drops of water at the high humidities. In general the deterioration has been slight. Electrose No. 8 is a more recent product, being one of several very similar samples which were submitted.

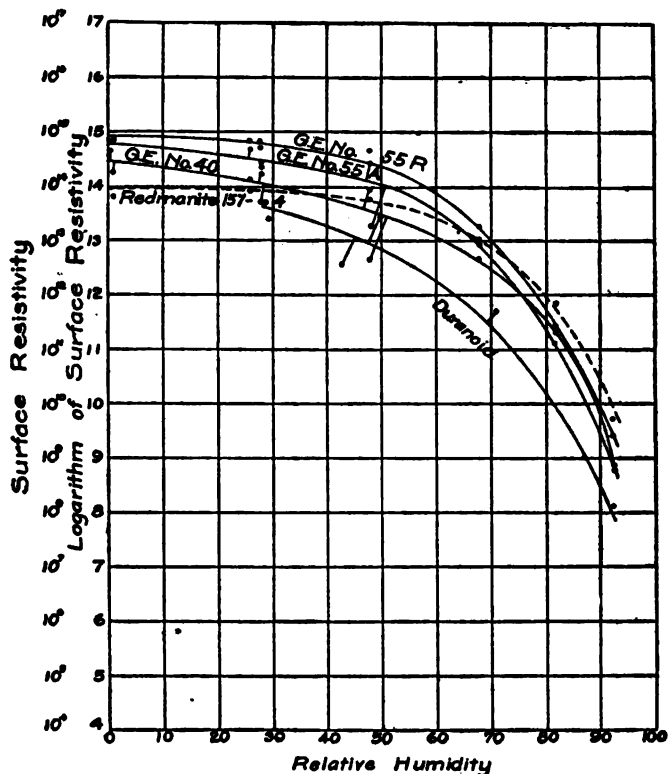


FIG. 19.—Change of surface resistivity with humidity of miscellaneous molding compounds

In Fig. 19 are shown the curves for duranoid, redmanite 157-4, and three materials submitted by the General Electric Co. The duranoid is from the Duranoid Manufacturing Co., of Newark, N. J. It closely resembles hard rubber in external appearance.

The samples G. E. 40, 55A, and 55R have also an appearance very much like hard rubber. They were exposed to the sunlight for four months without any effect that could be detected.

The sample of redmanite 157-4 was one of several samples submitted by Dr. Redman, of the University of Kansas. All have an amber-like appearance, though the color varies considerably. There was considerable variation in the surface resistivity, the one whose curve is given being among the best.

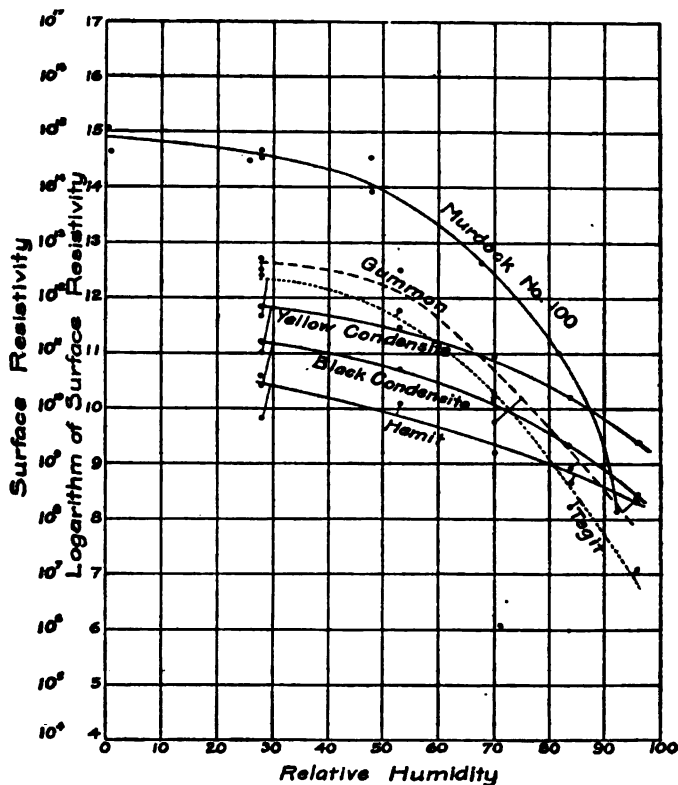


FIG. 20.—Change of surface resistivity with humidity of miscellaneous molding compounds

The samples in Fig. 20 are commercial insulators. The curve marked Murdock No. 100 is representative of several samples furnished by the J. W. Murdock Co., of Chelsea, Mass. The other samples gave curves which lie very close to the curve that is given. This is of considerable interest, since they are quite different in external appearance. However, they were all made either with shellac as a binder or with shellac mixed with some gum. A comparison of this curve with that of orange shellac given in Fig. 15 shows that they are almost identical. It would therefore appear that in certain cases the shellac forms the surface layer. In this connection it should be noted again that in the case of sealing wax, which is a mixture of shellac and rosin, the curve follows that of rosin more closely than shellac.

The gummon, tegit, and hemit are from the Hemming Manufacturing Co., of Garfield, N. J. They are coal-tar products.

The black and yellow condensite are from the Condensite Co. of America, Glen Ridge, N. J. They are phenol-condensation products combined with binders. It would appear in this case that the presence of the black coloring matter affects the surface resistivity.

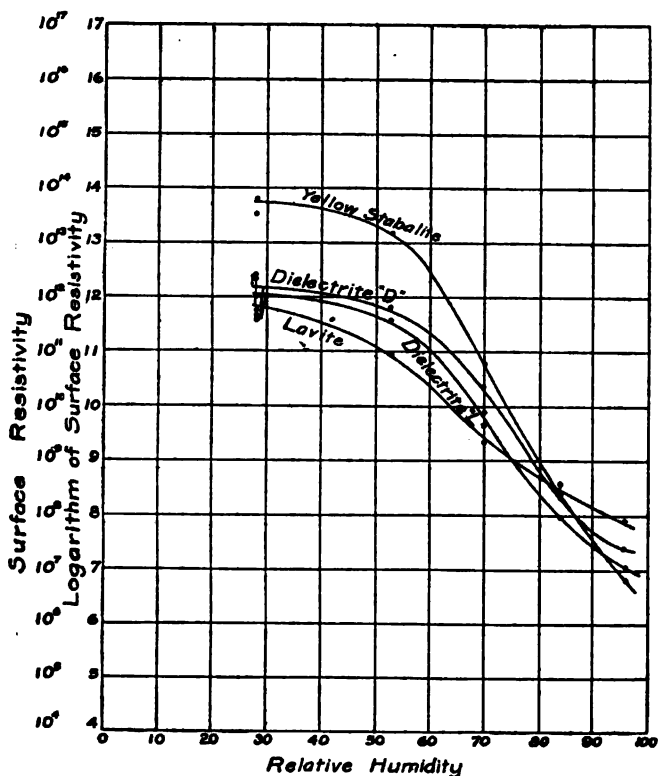


FIG. 21.—Change of surface resistivity with humidity of miscellaneous materials

In Fig. 21 are the curves for some miscellaneous materials. Stabalite is a rubber compound which is used to a considerable extent in Germany, but which has not found extensive use in the United States. It is manufactured by the Allgemein Elektrizitäts Gesellschaft, of Berlin, Germany. The samples of dielectrite were furnished by the Staunton Dielectrite Rubber Co., of Muskegon, Mich. The curves are given for two samples as showing what reproducibility may be expected between two samples of the same material. This was chosen as representing the difference that may be expected in samples which are of the same manufacture. These samples were not from the same piece, but were made at the same time in the same mold. Material made at different times according to the same method may have a somewhat larger difference. The results on the large number of insulators measured lead to the conclusion that the difference in the surface resistances of two samples of the same material at any humidity seldom varies by as much as a factor of 10.

The sample of lavite was furnished by the D. M. Steward Manufacturing Co., of Chattanooga, Tenn. It somewhat resembles unglazed porcelain. It is familiar to many from its extensive use in the tips of gas burners. The curve also resembles that of unglazed porcelain.

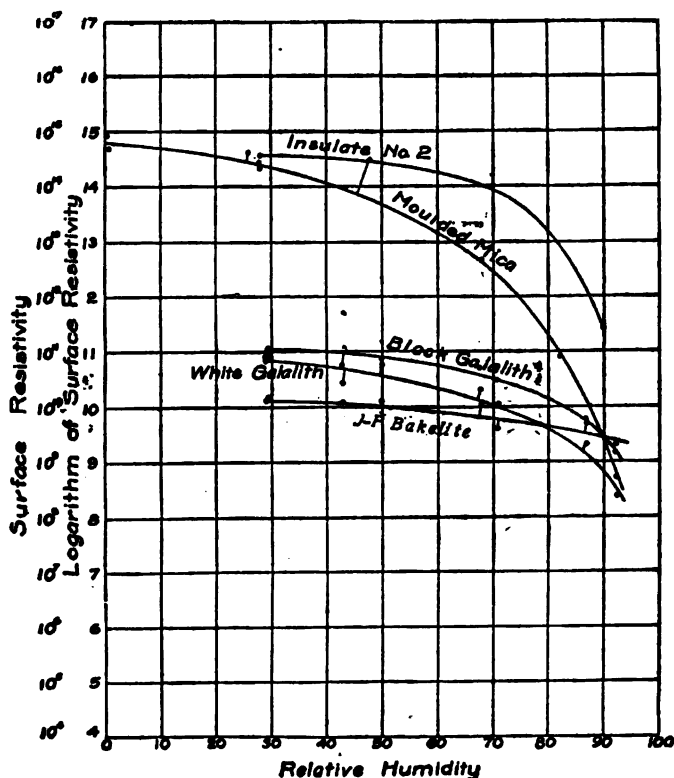


FIG. 22.—Change of surface resistivity with humidity of miscellaneous materials

In Fig. 22 are the curves of some miscellaneous materials. Insulate No. 2 is representative of several samples, all having nearly the same surface resistivity, which were furnished by the General Insulate Co., of New York. It is a moulding material, certain grades of which closely resemble hard rubber. Moulded mica and J-P Bakelite are also moulding materials, manufactured by the Johns-Pratt Co., Hartford, Conn. The moulded mica consists of ground mica and asbestos with shellac as a binder. It should be noted that, as in the case of the Murdock compounds, this curve corresponds very closely with the curve for shellac, showing that so far as surface effects are concerned they are almost entirely dependent upon the shellac. The sample was also exposed to sunlight for a period of four months without appreciable deterioration. The J-P Bakelite is a bakelite compound.

The samples of galalith were obtained from the International Galalith Gesellschaft, having factories in England, France, and Germany. The material is made from the casein of milk, and uncolored is being used as a substitute for ivory. For insulating purposes it is somewhat better than ivory. In this case the introduction of coloring matter evidently improves the surface leakage.

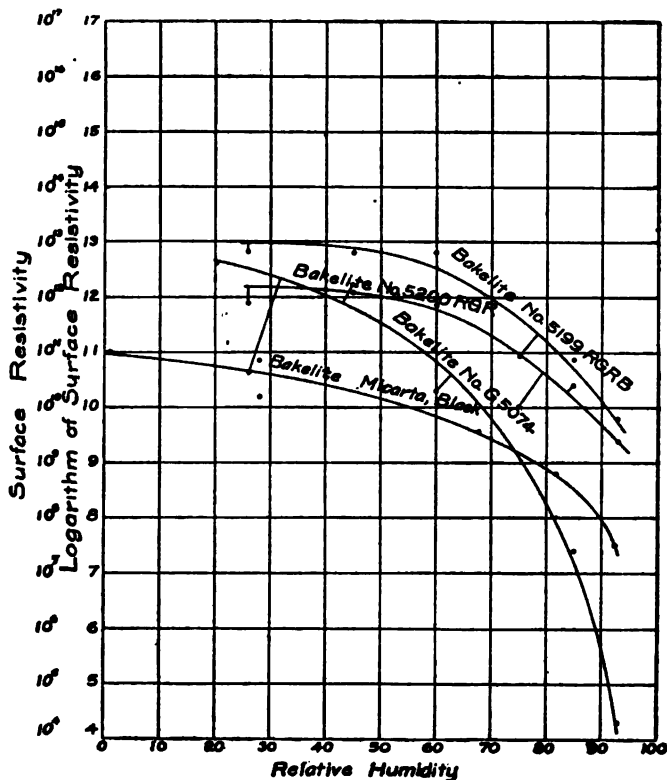


FIG. 23.—Change of surface resistivity with humidity of bakelite

In Figs. 23 and 24 are shown the curves for various samples of bakelite. The bakelite micarta was secured from the Westinghouse Electric & Manufacturing Co., of Pittsburgh. The other samples were furnished by Dr. Baekeland, of the General Bakelite Co., New York City. They furnish an interesting study of the effect of adding substances, portions of which may dissolve in the insulator.

The bakelite micarta is made in much the same manner as is indicated below for sample No. 1. It will be observed that the curves for these two materials have the same general form.

The curve of Fig. 24 for bakelite L558 shows a sample which has recently been produced by Dr. Baekeland and which he believes to be very pure bakelite, starting from phenol as a base. Its insulating properties are very good, and it shows relatively little change with humidity. The curve for bakelite, regular, is also for bakelite without a filling material. It was, however, made from cresol and ammonia was used as a catalytic agent. This shows how slight variations in composition may produce very pronounced effects in the surface resistivity. The composition and method of preparing the other samples is given in Table 4, page 399, which was furnished by Dr. Baekeland.

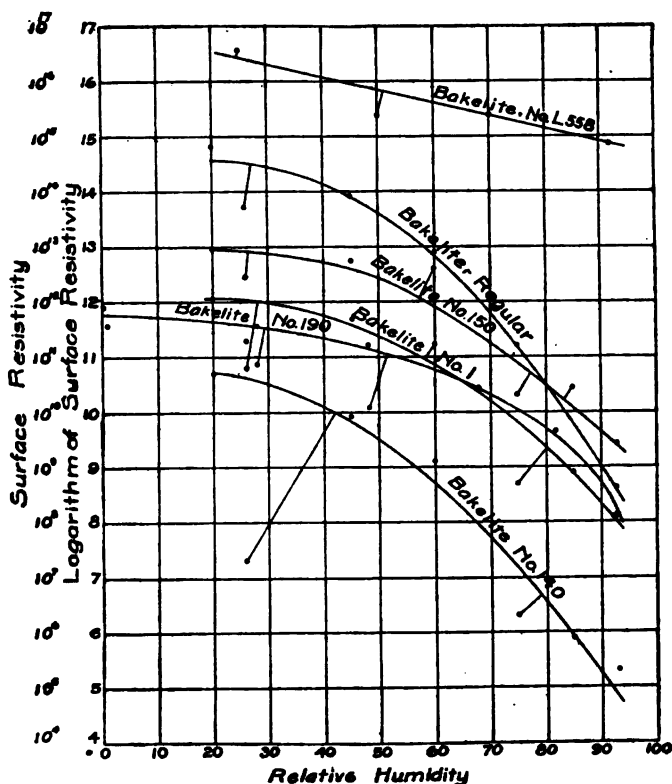


FIG. 24.—Change of surface resistivity with humidity of bakelite

In the curves for 140 and 150 is shown the effect of the catalytic or condensing agent. The curve of No. 140, in which caustic soda is the catalytic agent, lies below that of No. 150, in which ammonia is used as a catalytic agent. Evidently sufficient sodium salts remain on or near the surface to materially effect the condensation of water, and also the volume resistivity of the material is lowered by their presence. No. G. 5074 also contains sodium salts and, in addition, talcum as a binder. It shows very pronounced effects due to humidity. That water even penetrates into the material is shown by the curve of Fig. 5. No. 190 is similar to 150, except that cresol is used as a base. No. 5199 R. G. R. B. is the same as No. 150, but it was prepared with special care. There is but little difference between the curves of the two. No. 5200 R. G. R. is the same as No. 150, except that some china clay is used as a binder. The curves show that this has a deleterious effect.

From the above, certain conclusions can be reached. In the first place, the catalytic agent apparently has a marked influence on the final product. Also the nature of the binding material influences the surface resistivity. This is in contrast with the effect which was observed in the case of shellac.

TABLE 4

Table Showing the Composition of the Different Samples of Bakelite

Sample number	Per cent bakelite	Filling material	Phenolic body	Condensing agent	Method of preparing sample
1.....	?	Paper.....	Mixture of ortho-cresols, meta-cresols, and paracresols.	Ammonia.....	A composite cardboard impregnated homogeneously with bakelite varnish and hardened in the hot hydraulic press.
140.....	50	Vegetable fiber....	Phenol (C_6H_5OH).	Caustic soda..	Moulded in hot hydraulic press 160°-180° C.
150.....	50	do.....	do.....	Ammonia.....	Do.
190.....	50	do.....	Mixture of ortho-cresols, meta-cresols, and paracresols, and cyclic hydrocarbons.	do.....	Do.
5199 R. G. R..	50	do.....	Phenol (C_6H_5OH).	do.....	Do.
5200 R. G. R..	50	Mixture of vegetable fiber and china clay.	do.....	do.....	Do.
G. 5074.....	35	Talcum.....	do.....	Caustic soda..	Do.

2. EFFECT OF TEMPERATURE

The effect of change of temperature on the surface resistivity was investigated for a number of samples. From the preceding work it is apparent that the humidity must be maintained constant. From the work of Regnault it is found that the relative humidity of air in equilibrium with a sulphuric acid solution is almost independent of the temperature. Hence, it was only necessary to set the thermostat for a different temperature, since the change in the amount of moisture in the air necessary to maintain the relative humidity constant is automatically taken care of by the sulphuric acid solution.

The first attempt was made at a humidity of 25 per cent by changing the temperature from 25° to 30° C. From these measurements no change in the surface resistance with temperature was detected. However, at this humidity the current which flows through the volume of the dielectric is so large a part of the total

that determinations of the surface resistance are very inaccurate. The leakage resistance decreased in all cases, but in no case by more than a factor of two. This change is entirely accounted for by the change in the volume resistivity with temperature, data for which has already been given.

In order to obtain more accurate results upon the effect of temperature on the surface resistivity, samples were measured at 25° C and 94 per cent humidity, then the temperature increased to 31° C, keeping the humidity constant. A range of samples was chosen from very good insulators to poor insulators. In no case did the resistance vary by more than a factor of three, and in most cases it was much less. In some cases there was an increase in resistance, in others a decrease.

Hence, for practical work in the laboratory changes in surface leakage due to changes in temperature are of so little importance compared to the changes in resistance due to changes in relative humidity that they may be neglected. It is not to be supposed that this will hold for temperatures considerably removed from those used in this investigation.

EFFECT OF EXPOSURE TO LIGHT

Exposure to light may produce either a temporary or permanent effect. The temporary effect causes a change in surface leakage only while the light is shining on the surface. This was observed by Goldmann and Kalandyk⁸ in the case of sulphur and by Bates⁹ in the case of sulphur and ebonite. These results could not be reproduced in this laboratory.

Exposure to light may produce a chemical change at or near the surface which will be permanent. This chemical change may change the appearance of the material as well as the surface resistivity. However, there does not appear to be any connection between the two. Some samples, which show a very pronounced change in appearance, show very little change in surface resistivity and the reverse is sometimes the case.

The work under this head may be divided into two parts; (a) the effect of exposure to sunlight, and (b) the effect of exposure to

⁸ Ann. d. Phys. (4), 36, p. 589; 1911.

⁹ British Ass. Adv. Sci., 1909, p. 405, and by Le Radium, 8, p. 312; 1911.

ultra-violet light. The chemical changes produced by sunlight are usually much slower than those produced by ultra-violet light. Hence, it was possible to obtain effects in a few hours by means of ultra-violet light which would require months or even years to produce by sunlight. It must, however, be borne in mind that the results may not, in all cases, be identical. Hence, while the results found with ultra-violet light are valuable as indicating the chemical stability of the insulator, yet it is to be expected that in some cases the same changes will not take place in sunlight.

(a) **EFFECT OF SUNLIGHT**

As the chemical changes produced by sunlight take place very slowly, the number of specimens examined has been limited. The major portion of the work has been done upon hard rubber where the changes take place rather rapidly, though some work has been done upon more resistant materials.

(1) **Deterioration of Hard Rubber.**—For some years a study has been made of the effect of sunlight upon hard rubber. In Fig. 25 is a curve showing the deterioration with time of a sample of hard rubber exposed to sunlight. As the effect of humidity was not appreciated at the time the work was begun, the results must be considered qualitative rather than quantitative. However, as the measurements were always made at humidities less than 50 per cent, as simultaneous measurements upon a similar sample which had been kept in the dark never showed marked changes, and as two other samples from different sources gave similar results, it is improbable that a more careful study would yield results of great importance.

It will be noticed that the sample was prepared in January, 1907, and exposed to the diffuse light of the laboratory for nearly a year, when measurements were taken and marked deterioration noted. The sample was then exposed to sunlight, being placed vertically just inside a south window. In July, 1908, the resistance was very low and it was decided to see if the sample could be restored to its original condition by cleaning. That this was accomplished is shown by the measurements of December, 1908, when the resistance was somewhat higher than it was when the

sample was new. The method of cleaning is given in the following section.

The sample was then placed in the sun, and subsequent measurements showed that it decreased in resistance, but at a somewhat slower rate than in the previous case. This is in agreement with the results of Rayner.¹⁰

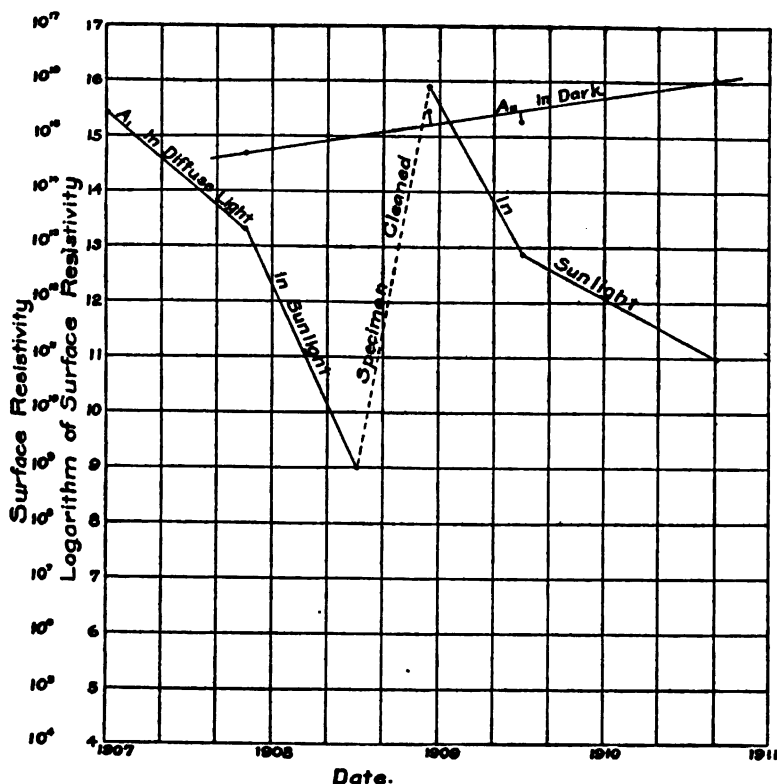


FIG. 25.—Deterioration of hard rubber by exposure to sunlight

The curves for the change of resistance of this sample with humidity taken after its removal from the sunlight in 1909 is given in Fig. 10 (American hard rubber in light). It shows very pronounced changes with humidity.

The cause of these changes is evidently in the chemical decomposition of the hard rubber by light. Hard rubber is formed by

¹⁰ Report of the National Physical Laboratory, p. 40; 1910.

vulcanizing Para rubber and sulphur, using about two-thirds rubber and one-third sulphur. There is also incorporated a large per cent of mineral filling material. When this rubber is exposed to light in the presence of air, complicated chemical reactions are set up which result in oxidizing the sulphur to the equivalent of sulphuric acid. This may take up ammonia from the air to form ammonia sulphate, or it may attack the filling material, forming sulphates of various kinds. Many of these sulphates are very hygroscopic, condensing water from the air to form a layer on the surface which is highly conducting due to the dissolved salts. Hence, the presence of these sulphates increases the amount of moisture and also increases its conductivity, so that the large decrease in resistance is readily explained.

(2) **Renovation of the surface of Hard Rubber.**—In view of the above considerations it is evident that if the sulphates are removed, the rubber should be restored to its original resistivity. However, several methods of cleaning were tried upon the samples above described before a satisfactory one was discovered. Rubbing with oil improved the insulation, but did not restore it to its original value. Cleaning with sodium hydroxide improved the appearance but not the insulation. Finally the samples were suspended in a vessel of distilled water and allowed to remain for two days. The results are shown in the measurements of December, 1908. It will be noticed that the resistance is somewhat higher than the original value. This is due to the fact that the surface has been somewhat roughened, thus making a longer leakage path.

In some later work it was found advisable to first wash the surface in a dilute solution of ammonia, then to wash it thoroughly with water. The surface should be wiped with a cloth until it is dry, then rubbed with a cloth moistened with light lubricating oil. The essential factor in improving the insulation is water, the other processes being used to improve the appearance of the sample.

(3) **Deterioration of Other Materials.**—In Fig. 18 are given results upon two samples of electrose which had been exposed to sunlight for more than two and a half years. The changes which took place were not very marked and appeared to be more physical than chemical. The surface of the black electrose after long exposure showed fine cracks, which doubtless explains the increase

in resistance of that specimen for low humidities. Both specimens showed slight discoloration, but there was no formation of salts on the surface as in the case of hard rubber.

Samples of moulded mica (this uses shellac as a binder, and its surface properties are almost identical with shellac) and of moulding compositions 55A, 55R, and 40 furnished by the General Electric Co., were exposed to sunlight for four months in the winter of 1912 and 1913. The curves after exposure were identical with those before exposure.

(b) **EFFECT OF EXPOSURE TO ULTRA-VIOLET LIGHT**

The effect of ultra-violet light in accelerating chemical action is well known. As the effect of light upon the surface resistivity is largely due to chemical action upon the surface layers, it seemed probable that those samples which deteriorate in sunlight would deteriorate much more rapidly in ultra-violet light. As this test could be applied in much less time than the test with sunlight, it seemed desirable to try it upon a number of samples.

The source of ultra-violet light was a quartz mercury vapor lamp taking 4 amperes on 118 volts. The specimens were placed about 12 inches below this lamp and exposed to the radiation for 19 or 20 hours. All the materials showed some change in appearance, except in the case of some samples of glass. The effect upon the surface resistivity was very different with different materials. Results upon six representative samples are given in the curves of Figs. 26 to 28. To make comparison easier, curves for the samples in their normal state are here given, and the curves obtained after exposure to ultra-violet light are plotted on the same sheets.

In Fig. 26 are given curves for hard rubber and for a specimen of hard rubber coated with bakelite. In both cases there was an interval of but one day between finishing the first curve and beginning the second. In that interval they were exposed to ultra-violet light for about 20 hours. The hard rubber has deteriorated as much as after several months exposure to strong sunlight.

The curves for the sample of hard rubber covered with bakelite are very interesting. The hard rubber was cut from the same piece as the sample mentioned above. It was covered with a thin coating of bakelite by Dr. Baekeland. Bakelite lacquer was

applied by spraying, then the sample air-dried, and finally baked for 12 hours at 120° C. The curves show that there was a decided improvement in the surface insulation¹¹ due to the thin coat of bakelite, especially at the higher humidities. However, when the sample had been exposed to ultra-violet light for 20 hours, the surface resistivity at the higher humidities was less than one-ten

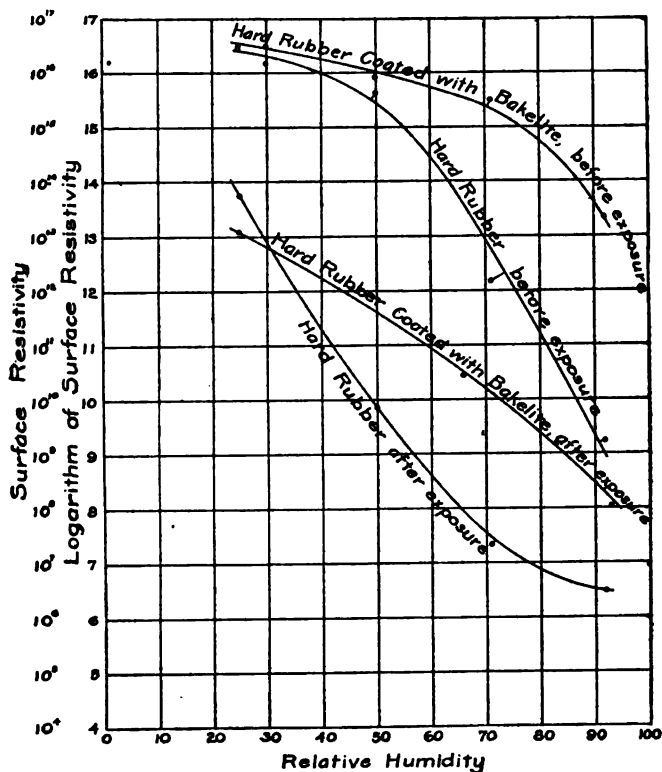


FIG. 26.—Change of surface resistivity with humidity of hard rubber and hard rubber coated with bakelite both before and after a 20-hour exposure to ultra-violet light

thousandths of the value before exposure. The relative decrease was somewhat larger than for the hard rubber. The exposed surface of the bakelite covered sample appeared but little different to the naked eye than the unexposed surface, but under a microscope the exposed surface appeared covered with innumerable

¹¹ This was observed by Wömmeldorf, who uses this material in constructing a new type of electrostatic machine. See *Electrotech Zs.*, 85, p. 61; 1914.

very fine blisters. Whether a like effect would take place if the sample was exposed to sunlight can be ascertained only by experiment. Such experiments are now in progress.

In Fig. 27 are results upon glyptol and moulded mica. The curves showing the surface resistivity before exposure to ultra-violet light are the same as those previously given. The other curves were after exposure to ultra-violet light for 20 hours. The

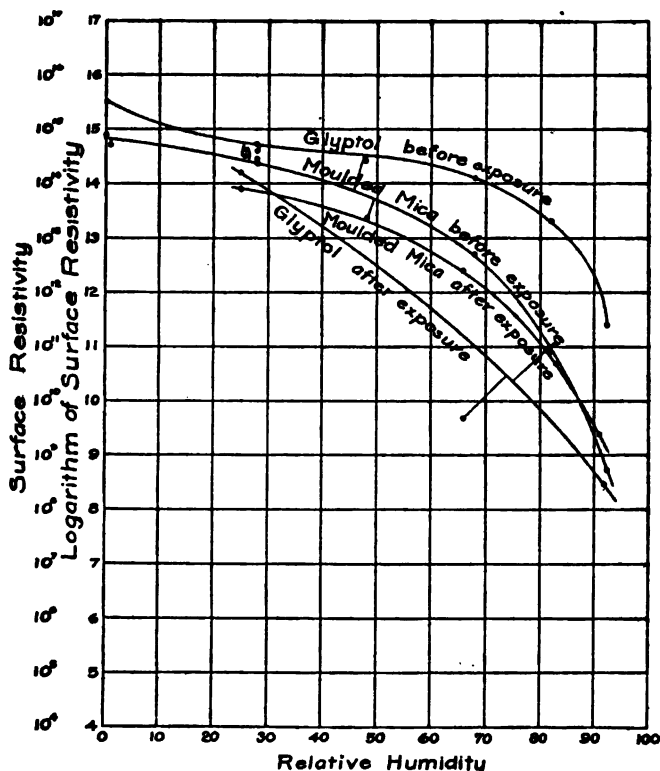


FIG. 27.—Change of surface resistivity with humidity of glyptol and moulded mica both before and after a 20-hour exposure to ultra-violet light

difference in the case of moulded mica (a compound using shellac as a binder) is small; and since the curves are not for the same sample, it is quite possible that no change whatever has taken place.

In the case of glyptol, however, the change is very marked. Since glyptol is a synthetic compound which has the appearance

and many of the properties of amber, it seemed possible that amber itself would be affected by ultra-violet light. Experiment showed that this is the case, though it was not so pronounced as in the case of glyptol.

In Fig. 28 are shown the results upon bakelite and electrose. The electrose is not the same as that whose curves showing the

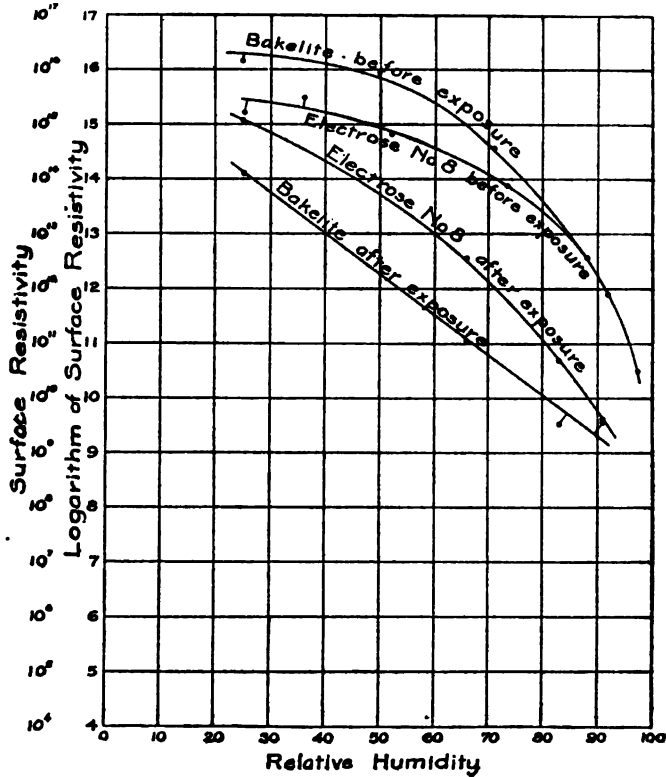


FIG. 28.—Change of surface resistivity with humidity of bakelite and electrose both before and after 20 hours' exposure to ultra-violet light

effect of sunlight are given in Fig. 18, though it is doubtless similar. The deterioration for 20 hours in ultra-violet light is as great as in sunlight for several years. The curves of bakelite are those of a single sample. It had very high surface resistivity before exposure to ultra-violet light, being among the best samples furnished by Dr. Baekeland. There was an appreciable deterioration due to the exposure to ultra-violet light.

Besides the materials quoted above, a number of other samples were studied. No attempt was made to examine all the samples. To give an idea of the changes which take place, Table 5 was prepared. In the second column of this table are given values of the surface resistivity measured at 90 per cent humidity after exposure to ultra-violet light for 20 hours. In the third column are given the values of the factor by which the surface resistivity after exposure must be multiplied to give the surface resistivity before exposure.

TABLE 5

Effect of 20 Hours Exposure to Ultra-violet Light upon Surface Resistance

[Temperature, 25° C; humidity, 90 per cent]

Materials which showed pronounced decreases	Surface resistivity after exposure	Factor by which resistance decreased	Materials which showed slight changes	Surface resistivity after exposure	Factor by which resistance decreased
Hard rubber covered with bakelite*.....	4.6×10^9	48 000	Moulded mica.....	1.4×10^9	5.7
Glyptol.....	4.4×10^7	45 000	White celluloid.....	9.1×10^8	4.8
Bakelite No. L 530x.....	1.7×10^{10}	35 000	Bakelite No. G 3622.....	3.3×10^8	1.5
Electrose No. 8.....	4.2×10^9	380	Bakelite No. G 3623.....	1.3×10^9	1.4
Hard rubber*.....	6.4×10^8	280	Bakelite No. G 3618 a.....	1.1×10^8	1.2
Bakelite No. L 530y.....	3.8×10^9	260	Gumman.....	1.9×10^8	1.2
Insulate No. 2.....	1.6×10^9	190	G. E. No. 55 R.....	1.1×10^{10}	1
Italian marble.....	1.7×10^8	36	Moulded mica.....	2.5×10^8	1
Bakelite No. G 3618b.....	3.5×10^9	27	Brown glass.....	7.1×10^7	0.8
Amberite.....	1.2×10^{10}	12	Clear glass.....	2.9×10^9	0.8
			Murdeck No. 200.....	1.1×10^9	0.2

* The "hard rubber covered with bakelite" was cut from the same sample as the "hard rubber."

The results may be divided into two classes—those which show a decrease in surface resistivity and those in which there is no change. The table is arranged so that not only are these classes shown, but also the materials in the first class are arranged in the order of their relative change. While these results can not be taken as indicating that if the substances were exposed to sunlight for a sufficiently long time, the change in surface resistance would be the same relatively as that given in the table, yet the results upon the few substances which have been examined point in that direction.

4. NATURE OF SURFACE LEAKAGE

We have assumed that surface leakage is due to a film of moisture or other conducting material on the surface of the insulator. If this is the case, it should be possible to find some connection between the thickness of the film, the conductivity of material of which it is composed, and the surface resistivity. In the case of quartz and various kinds of glass, the thickness of the water film condensed upon the surface when a sample is placed in a humid atmosphere has been determined by weighing. It should, therefore, be possible to determine the conductivity of the water in the film and see if this is a value such as might be expected.

Ihmori¹² found that the thickness of the film on cleaned quartz at about 90 per cent humidity is from 0.003 to 0.006 micron (3 to 6×10^{-8} mm). With uncleaned specimens he found the thickness to be from 0.014 to 0.062 micron. Briggs¹³ found at 85 per cent a thickness of 0.0045 micron of water on a quartz surface and of 0.027 micron at 99 per cent humidity. If the value of the thickness is taken as 0.06 micron (the highest measured value) and the surface resistivity as 10^{-8} ohms (the lowest value measured), the conductivity of the water is 0.0017 mho per cm. Since quartz is practically insoluble, the conductivity is largely due to soluble salts on the surface.

If this conductivity is due to the presence of sodium chloride, there must be present on each square centimeter of surface 6×10^{-9} gram of the salt. It is evident that cleaning must be done with great care to exclude such minute quantities of impurities.

Besides soluble salts on the surface, there may be gases condensed from the air which will affect the conductivity. Those most to be expected are ammonia and carbon dioxide. Under the conditions of this experimental work, the ammonia would be rapidly absorbed by the sulphuric acid used to control the humidity. To insure the absorption of the carbon dioxide, a solution of potassium hydroxide was made, the vapor pressure of which was such as to give a humidity of 95 per cent in the surrounding air. This was used in conjunction with a sulphuric acid solution

¹² Wied. Ann., 81, p. 1006; 1887.

¹³ J. Phys. Chem., 9, p. 617; 1905.

having the same vapor pressure. The results obtained showed that even in the case of cleaned quartz the carbon dioxide absorbed from the air has very little effect on the resistivity.

In the case of the cleaned quartz, the surface resistivity is about 10^{12} ohms at 90 per cent humidity, and, from the work quoted, the thickness of the water layer is about 0.005 micron. The conductivity of the water is then 2×10^{-8} mho per cm. This is of the same order of magnitude as the conductivity of distilled water.

In the case of glass, it is well known that certain salts from the glass dissolve in water. Hence, cleaning glass will not be expected to produce the same effect as in the case of quartz. Experiment has shown this to be the case. Soft glasses are very little affected by cleaning, but the more insoluble glasses show considerable change after thorough cleaning, but this is in no case as pronounced as in the case of quartz.

Parks¹⁴ finds that the thickness of the water film on glass is about 0.1 micron. The lowest measured value of the surface resistivity of glass recorded in this paper is 2×10^7 ohms. This gives a value of the conductivity of the water 5×10^{-3} mho per cm, or a volume resistivity of 200 ohm-cm. This can be explained by the solubility of the glass in water.

Amber is a very insoluble substance, and the effect of cleaning is quite as marked as in the case of quartz. However, no data on the thickness of the surface film has come to the notice of the author.

Attention has been called to the fact that in the case of hard rubber at very low humidities the presence of salts on the surface does not affect the surface leakage. It appears, therefore, that the surface leakage at higher humidities is due to a film of water in which the salts are dissolved.

In the case of the waxy materials, the angle of contact between water and the material is greater than 90° . If water is condensed upon the surface of one of these materials it tends to draw into drops, instead of spreading over the surface. Hence, it would be expected that the leakage resistance of waxy materials would be

¹⁴ *Phil. Mag.*, (6) 5, p. 517; 1903.

very little affected by a change in humidity. That this is the case has already been shown. From measurements of the resistance, the presence of a surface film on these materials can not be detected.

From the cases which have been cited, it appears that when placed in an atmosphere having high humidity the decrease in the surface resistance of insulators is due to the condensation of moisture on the surface. Any condition which will affect either the amount of moisture on the surface or its conductivity will affect the surface leakage. Hygroscopic salts will increase the thickness of the water film, and any soluble salt will increase its conductivity. Hence the presence of inorganic salts on the surface of an insulator produces a decrease in the surface resistivity. Since the quantity of water in the surface film is very small, the amount of salt required to produce very large changes in the surface resistivity is exceedingly minute.

Besides water films, thin films of oil are often present on the surface of insulators. The volume resistivity of oil is much higher than water. The values found in this laboratory range from 10^{11} to 10^{18} ohm-centimeters for good mineral oil, and from 10^8 to 10^{12} for animal and vegetable oils.

If we assume that the thickness of the oil film is 0.1 micron and that the resistivity of the oil is 10^{11} ohm-centimeters, the surface resistivity would be 10^{10} ohms. Since very few of the curves go above this value, it seems probable that the surface resistivity is generally limited by the resistance of a film of oil on the surface of the insulator. The only exceptions are the waxy materials.

5. METHODS OF COMPUTING SURFACE RESISTIVITY

The surface resistance must always be computed from measurements of the leakage resistance and volume resistivity. In the great majority of cases the current which flows through the solid is such a small part of the total that the surface resistance does not differ from the leakage resistance by as much as the error of measurement. However, at very low humidities this may not be the case. The resistance which the solid insulator offers to the flow of current can be computed for certain forms of electrodes, and in these cases the surface resistance can be obtained. One

case which can be solved is that of two narrow strips of conductors placed upon the surface of an insulator.¹⁵

If two strips of width a cm and of infinite length are so pressed upon the surface of an insulator of infinite surface and thickness that the distance between their inner edges is b cm, the resistance, R , per unit length between these strips is—

$$R = \frac{2K}{K'} \rho$$

where K and K' are the complete elliptic integrals¹⁶ of the first kind to the moduli k and k' respectively, where $k = \frac{b}{b+2a}$ and $k' = \sqrt{1-k^2}$.

From this formula the first four values in Table 6 have been computed. In three respects the above differs from the form which we have employed. Strips of infinite length have not been used, but it has already been noted that the correction on this account is negligible. The insulator is of finite breadth as well as length. But as very little of the current will flow in the region outside the strips, the correction on this account is negligible. The insulator is of finite thickness, and it is on this account that the only appreciable correction will enter.

Another case which can be solved is that of two infinitely wide strips upon an insulator of infinite thickness¹⁷ except at a point midway between the conductors.

The shape will be seen from Fig. 29. If two conductors, each infinitely wide and long, are placed b cm apart on an insulator of infinite thickness, but having a slit to within c cm of the top surface at a point midway between the conductors $R = \frac{2K'}{K}$

where in this case $k = \frac{c}{4b^2+c^2}$ and therefore $k' = \frac{2b}{4b^2+c^2}$.

Values for different thicknesses calculated by the two formulas are given in Table 6.

¹⁵ The corresponding problem in electrostatics was solved by J. J. Thomson. (See *Recent Researches in Electricity and Magnetism*, p. 238.) It is only necessary to interpret the result given by Thomson in terms of resistance instead of capacity.

¹⁶ Tables of the numerical values of these integrals can be found in Legendre's *Traité des Fonctions Elliptiques*, volume 2, and in this Bulletin, 8, p. 202, Reprint 169. The value can, however, be computed with much greater precision than is demanded by this work from the relation $\frac{K}{K'} = \left(\frac{1+k'}{1+k}\right)^2$.

¹⁷ The corresponding case in electrostatics is given by J. J. Thomson. *Loc. Cit.*, p. 243.

TABLE 6

Table showing the Resistance between two Strips on the Surface of an Insulator if all of the Current flows through the Body of the Insulator

Width of strip (a)	Distance between strips (b)	Thickness of insulator at center (c)	Resistance
cm	cm	cm	$\rho = \text{volume resistivity}$
0.01	1	∞	3.9ρ
0.1	1	∞	2.4ρ
1.0	1	∞	1.3ρ
10.0	1	∞	0.7ρ
∞	1	1.0	2.7ρ
∞	1	0.5	3.6ρ

While at first this seems to be very different from the case we are considering, yet a consideration of the lines of flow will show that the removal of the portion outside the dotted lines in Fig. 29 will not greatly change the resistance.

From a consideration of these values we have concluded that, for the samples which have been used in this investigation, the resistance of the body of the insulator is three times the volume resistivity of the material. Some experimental work where the surface film was reduced to a minimum gave 3.3. Hence, for the order of accuracy which can be attained

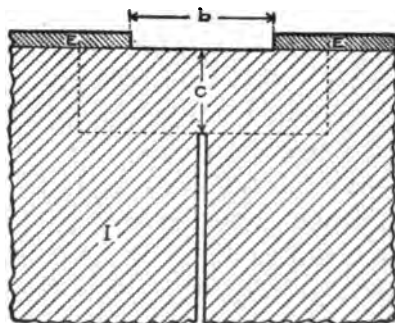


FIG. 29.—Diagram showing an insulator of such form that the resistance between the electrodes can be computed

in this work, it is sufficient to say that the resistance of the body of the insulator is three times the volume resistivity of the material.

Since the leakage resistance per unit length, r , consists of the surface resistance and volume resistance in parallel, it follows that the surface resistivity σ is given by the equation

$$\sigma = \frac{3r\rho}{3\rho - r}$$

where r is the leakage resistance per unit length.

If 3ρ is large relative to r , then $\sigma=r$ and σ is determined with the same accuracy as r . But when r approaches in value 3ρ , σ becomes very large and errors in either r or ρ will introduce much larger errors in σ . It is therefore at the low humidities where σ is large that the values are most inaccurate. Fortunately, it is in this region that precise values are of the least importance in practical work.

When this work was in progress and the curves constructed, the necessity for applying the correction outlined above was not appreciated. From the results which have already been given showing the factors which affect both the volume resistivity and the surface resistivity, it will be seen that it is possible to make an accurate determination of the surface resistivity only when the leakage resistivity and volume resistivity are measured at the same time. As it is only at low humidities that the correction is appreciable and as at these humidities the surface leakage is seldom of importance, the curves showing the change of surface resistivity with humidity have not been changed. However, in order to show the magnitude of the correction in the most unfavorable cases, Table 7 has been prepared.

In this table are given the measured values of the volume resistivity and the leakage resistivity at low humidity. The surface resistivity at low humidity computed from these values is given in the third column. Those in which r is larger than 3ρ give negative values of σ , while those in which r equals 3ρ give infinite values of σ . Such values of σ can only be accounted for by errors in the value of either r or ρ . The values of ρ are a weighted mean of several different samples measured at different times. The values of r are from a curve for one sample which was chosen as representative of several samples measured. Hence, it is not surprising that the values of r and ρ can not in all cases be used in computing σ .

TABLE 7

Table Giving Values of the Volume Resistivity, the Leakage Resistivity, and the Surface Resistivity at Low Humidities

[Humidities 20 per cent or less. ρ —Volume resistivity; r —Leakage resistivity; σ —Surface resistivity]

Sample	ρ	r	σ
Galalith, white	1×10^{10}	7×10^{10}	*
Yellow condensite	1×10^{11}	6×10^{11}	*
Black condensite	4×10^{10}	20×10^{10}	*
White celluloid	2×10^{10}	10×10^{10}	*
Bakelite No. 1	2×10^{11}	10×10^{11}	*
Bakelite No. 190	1×10^{11}	5×10^{11}	*
Galalith, black	2×10^{10}	10×10^{10}	*
Plate glass	2×10^{13}	6×10^{13}	*
Hemlit	1×10^{10}	3×10^{10}	*
Bakelite 5200 R. G. R.	4×10^{11}	10×10^{11}	60×10^{11}
Bakelite 5199 R. G. R. B.	5×10^{12}	10×10^{12}	30×10^{12}
Tetrachloronaphthalene	5×10^{13}	10×10^{13}	30×10^{13}
Bakelite No. 150	4×10^{13}	8×10^{13}	24×10^{13}
Bakelite No. L 558	2×10^{14}	3×10^{14}	9×10^{14}
Gumman	3×10^{13}	4×10^{13}	7×10^{13}
Yellow stabilite	4×10^{13}	5×10^{13}	9×10^{13}
J-P Bakelite	2×10^{10}	2×10^{10}	3×10^{10}
Dielectrite	5×10^{13}	6×10^{13}	10×10^{13}
Tegit	2×10^{13}	2×10^{13}	3×10^{13}
Bakelite mica	5×10^{16}	5×10^{16}	8×10^{16}
Moulded mica	10×10^{14}	7×10^{14}	9×10^{14}
G. E. No. 55A	10×10^{14}	5×10^{14}	6×10^{14}
Redmonite No. 157, 4	2×10^{14}	1×10^{14}	1×10^{14}
G. E. No. 40	10×10^{14}	3×10^{14}	3×10^{14}
Glyptol	10×10^{15}	2×10^{15}	2×10^{15}
Electrose No. 8	20×10^{15}	4×10^{15}	4×10^{15}
Yellow electrose	5×10^{15}	1×10^{15}	1×10^{15}
Murdock No. 100	30×10^{14}	5×10^{14}	5×10^{14}
Insulate No. 2	80×10^{14}	4×10^{14}	4×10^{14}
Black electrose	100×10^{13}	5×10^{13}	5×10^{13}
Amberlite	50×10^{15}	2×10^{15}	2×10^{15}
G. E. No. 55R	400×10^{14}	7×10^{14}	7×10^{14}

* Due to error in the determination of either ρ or r , or both, the value of σ cannot be computed. When r is of nearly the same value as ρ , small errors in either r or ρ will produce large errors in σ .

All of the materials in which the difference between r and σ is large have volume resistivities less than 10^{14} and the majority less than 10^{12} . Where the volume resistivity is as low as this, a knowledge of the surface resistivity will seldom be of importance. For humidities greater than about 25 per cent the surface resistance is the same as the leakage resistance except in the case of the waxy

materials. It is quite probable that for these materials a surface film does not exist, so that the surface resistivity is infinite.

In the preceding discussion it has been assumed that the air which is above the solid dielectric is a perfect insulator. This is true except in so far as the air is ionized. Hence, the current that flows through the air depends only on the number of ions present provided the potential gradient is sufficiently high to cause them to travel toward the electrodes. When the potential is applied, the ions which are already present are immediately carried to the electrodes, so that the continuous current depends on the rate of production of ions. The natural rate of ionization of the air is about 6 ions per second per cubic centimeter of air. The charges carried by these ions are approximately 10^{-18} coulomb. If we assume that the ions from 10 cm^3 of air will be drawn to unit length of the plates, the total current due to air conduction is only 10^{-17} ampere, which is quite negligible in comparison to the surface leakage of most materials. However, in case currents of air are passing over the dielectric the electric current through the air may be much larger, since the number of ions normally found in a cm^3 of air varies from 1000 to 2000. If the air over the specimen is completely changed 10 times per second, the current will become 3×10^{-14} ampere, an amount which becomes of the same magnitude as the surface current for the best specimens. Also the presence of any ionizing agent such as radium, Roentgen rays or ultra-violet light will increase the ionization and hence the current.

V. SUMMARY

1. Methods of measuring very high resistances are discussed, and diagrams given showing how they may be applied to the measurement of volume resistivity and surface resistivity.
2. The volume resistivities of more than 60 materials are tabulated. The effect of the humidity of the surrounding air, of the temperature of the specimen, and of the magnitude and length of application of the impressed voltage is discussed.
3. The surface resistivity is shown to be due to a surface film, usually of water or oil, on the insulator. This is generally the important factor in determining the leakage between two conduc-

tors insulated by a solid dielectric. However, for insulators having a volume resistivity less than 10^{14} ohm-centimeters placed in an atmosphere having an humidity less than 25 per cent, the greater part of the current may flow through the body of insulator.

4. The surface resistivity of most materials changes through wide limits when the humidity of the surrounding air is varied. It is often a million times as great at low humidity as at high humidity. About 75 curves are given showing the change of surface resistivity with humidity for various materials. The effects of temperature and of exposure to light are also treated.

In conclusion, I wish to recognize valuable assistance from my coworkers in the Bureau of Standards. I would especially mention Mr. Maxwell James who has made many of the measurements upon volume resistivity. I wish also to thank those firms who cooperated by furnishing materials.

WASHINGTON, June 8, 1914.

APPENDIX

TABLE 8

Volume Resistivity of Solid Dielectrics (materials listed alphabetically)

Material	Bureau of Standard's values	Values ¹⁸ of other observers		
	Resistivity at 22° C., ohm-cen- timeters	Resistivity, ohm-cen- timeters	Tem- pera- ture	Observer and reference
Amberite	5×10^{16}			Dietrich, Diss. Göttingen, 1909. Do. Addenbrooke, Electr., 66, p. 629; 1911.
Bakelite No. 1.....	2×10^{11}			
Bakelite No. 140.....	2×10^7			
Bakelite No. 150.....	4×10^{13}			
Bakelite No. 190.....	1×10^{11}			
Bakelite No. L558.....	2×10^{16}			
Bakelite No. G5074.....	4×10^{10}			
Bakelite No. 5199RGRB.....	5×10^{13}			
Bakelite No. 5200RGR.....	4×10^{11}			
Bakelite mica.....	5×10^{10}			
Beeswax:				
Yellow.....	20×10^{14}	8×10^{14}	20	
White.....	6×10^{14}	5×10^{14}	22	
Celluloid, white.....	2×10^{10}	4×10^{10}	16	
Carosin.....	Over 5×10^{10}			
Condensate:				Rayner, J. I. E. E., 34, p. 620; 1905.
Black.....	4×10^{10}			
Yellow.....	4×10^{10}			
Dielectrite.....	5×10^{13}			
Duranoid.....	3×10^{14}			
Electrose:				
No. 8.....	200×10^{14}			
Black.....	1×10^{14}			
Yellow.....	50×10^{14}			
Fiber:				
Hard.....	20×10^9			
Red.....	5×10^9	0.1×10^9	20	
Galalith:				
Black.....	2×10^{10}			
White.....	1×10^{10}			
G. E. No. 40.....	1×10^{14}			
G. E. No. 55A.....	1×10^{14}			
G. E. No. 55R.....	40×10^{14}			

¹⁸ When necessary the values have been reduced to the units given in the table.

Volume Resistivity of Solid Dielectrics (materials listed alphabetically)—Continued

Material	Bureau of Standard's values	Values ¹² of other observers		
	Resistivity at 22° C., ohm-centimeters	Resistivity, ohm-centimeters	Temperature	Observer and reference
Glass:				
German.....	5×10^{12}	0.05×10^{12}	18	Campbell, Phys. Sec., Lond., 25, p. 336; 1913.
Kavaller.....	800×10^{12}	1000×10^{12}	17	Thornton, Phil. Mag. (6), 19, p. 403; 1910.
Opal.....	0.1×10^{12}			
Plate.....	2×10^{12}			
Ordinary.....		9×10^{12}	20	Tables of French Phys. Soc.
Bohemian.....		0.6×10^{12}	20	Do.
Glyptol.....	1×10^{10}			
Gumman.....	3×10^{12}			
Halewar No. 1001.....	2×10^{12}			
Halewar No. 5055B.....	2×10^{12}			
Hard rubber.....	1×10^{12}	0.002×10^{12}		Curie, Ann. Chem. Phys. (6), 12, p. 203; 1889.
Do.....		0.03×10^{12}	Room.	French Phys. Soc.
Hemlit.....	1×10^{10}			
Insulate No. 2.....	8×10^{12}			
Ivory.....	2×10^{10}			
Khetinsky cement.....	2×10^{12}			
Levite.....	2×10^{10}			
Marble:				
Italian.....	100×10^9	10×10^9	Room.	Do.
Pink Tennessee.....	5×10^9			
Blue Vermont.....	1×10^9			
Mica:				
Do.....		9×10^{12}	20	Curie.
Black spotted African.....	0.04×10^{12}			Reed, Amer. J. Sci. (4), 14, p. 161; 1902.
Brown African, clear.....	2×10^{12}			
Colorless.....	200×10^{12}			
India ruby, stained.....	0.05×10^{12}	0.02×10^{12}		Wilson and Mitchell, Electr., 54, p. 880; 1905.
India ruby, alighty stained.....	50×10^{12}	0.04×10^{12}		Do.
Moulded mica.....	1×10^{12}			
Murdeck No. 100.....	3×10^{12}			
Paraffin (special).....	{ Over 500×10^{12}			
Paraffin (parowax).....				
Paraffin.....	1×10^{12}	300×10^{12}		Braun, Wied. Ann., 31, p. 870; 1887.
Do.....		5×10^{12}	17	Thornton, Phil. Mag. (6), 19, p. 403.
Do.....		{ 3 to 300×10^{12}	Room.	French Phys. Soc.
Do.....				
Porcelain, unglazed.....	3×10^{12}			

¹² When necessary the values have been reduced to the units given in the table.

Volume Resistivity of Solid Dielectrics (materials listed alphabetically)—Continued

Material	Bureau of Standard's values	Values ¹⁸ of other observers		
	Resistivity at 22° C, ohm-centimeters	Resistivity, ohm-centimeters	Temperature	Observer and reference
Quartz:				
to axis.....		2×10^{14}	17	Thornton.
Do.....		1×10^{14}	20	Curie.
⊥ to axis.....		200×10^{14}	17	Thornton.
Do.....		300×10^{14}	20	Curie.
Fused.....	{ Over 5×10^{13} }			
Redmonite, 157-4.....	2×10^{14}			
Resin.....	5×10^{13}	0.7×10^{13}	17	Thornton.
Sealing wax.....	8×10^{13}	1×10^{13}	19	Dietrich.
Shellac.....	1×10^{13}	0.9×10^{13}	Room.	French Phys. Soc.
Slate.....	1×10^8	2×10^8	Room.	Do.
Stabalite.....	3×10^{13}			
Sulphur.....	1×10^{17}	0.08×10^{17}	17	Thornton.
Tegit.....	2×10^{13}			
Tetrachloronaphthalene.....	5×10^{13}			
Vulcabeston ¹⁹	2×10^{10}			
Wood, paraffined.....		5×10^{10}	Room.	French Phys. Soc.
Mahogany.....	4000×10^{10}			
Maple.....	3×10^{10}			
Poplar.....	50×10^{10}			
Walnut.....		{ 0.09 to 1×10^{10} }		{ E. Muller, Electrotech. Zs., 13, p. 72; 1892.

¹⁸ When necessary the values have been reduced to the units given in the table.¹⁹ Vulcabeston should read "J-P Bakelite."

A DIRECT-READING INSTRUMENT FOR MEASURING THE LOGARITHMIC DECREMENT AND WAVE LENGTH OF ELECTROMAGNETIC WAVES

By Frederick A. Kolster

1. INTRODUCTION

The laws of the United States governing radio communication specify, among other things, that at all stations the logarithmic decrement per complete oscillation in the wave trains emitted by the transmitter shall not exceed two-tenths, except when sending distress signals or messages relating thereto.

The importance of the regulation lies in the fact that when persistent oscillations of single frequency are emitted from a radio transmitting station much more selective receiving apparatus may be employed with advantage at receiving stations, permitting sharp tuning with consequent minimizing of interference caused by stations other than those with which communication is desired.

Since the logarithmic decrement is a measure of the decay of a train of waves, it is desirable that this decrement be made as small as possible in order that a series of decaying trains of waves may approach as near as possible to the condition of persistent oscillations. A wave train having a logarithmic decrement of two-tenths, the limit set by the Federal regulations, will have 24 complete oscillations before the amplitude of the last wave has decreased to 1 per cent of that of the first. Such a wave train is shown in Fig. 1.

When full advantage is taken of the rapid scientific and technical progress which has been made in the methods of transmission of electromagnetic waves it is not at all difficult to comply with this requirement. In fact, it is practicable as well as desirable to keep well within this limiting value of two-tenths.

The product of the damping factor and period of one complete oscillation, αT , is called the logarithmic decrement and is commonly represented by δ .

Hence,

$$I = I_0 e^{-\alpha t}$$

and

$$\delta = \log_e \frac{I_0}{I}$$

The logarithmic decrement can also be written in terms of the constants of the circuit, for since $\alpha = \frac{R}{2L}$

$$\delta = \frac{R}{2L} T$$

$$= \frac{R}{2L n}$$

$$= \pi \frac{R}{L \omega}$$

$$= \pi R C \omega$$

The expression for the logarithmic decrement can also be derived by the following approximate method, which does not involve the solution of the differential equation:

The damping in a circuit is due to the dissipation of energy, and if we call R the total equivalent resistance, including the effect of electromagnetic radiation, the energy dissipated in one period is $R \bar{i}^2 T$, where $\bar{i}^2$ is the mean square current. In an undamped sine wave $\bar{i}^2$ is $\frac{1}{2} I_0^2$. For the case shown in Fig. 3, we may put approximately,

$$\bar{i}^2 = \frac{1}{2} I_1^2 = \frac{1}{2} I_0 I_2$$

The total energy at the beginning of the period is $\frac{1}{2} L I_0^2$ and at the end $\frac{1}{2} L I_2^2$. The energy dissipated during one period is therefore the difference.

By definition, the logarithmic decrement is

$$\delta = \log \frac{I_0}{I_1}, \text{ or } \frac{I_0}{I_1} = e^\delta$$

hence

$$\begin{aligned} 2\delta &= \log \frac{I_0^2}{I_1^2} = \log \frac{\frac{1}{2}LI_0^2}{\frac{1}{2}LI_1^2} = \log \left(\frac{\frac{1}{2}LI_0^2 + \frac{1}{2}RI_0I_1T}{\frac{1}{2}LI_1^2} \right) \\ &= \log \left(1 + \frac{RI_0T}{LI_1} \right) = \log \left(1 + \frac{RI_0}{LnI_1} \right) \end{aligned}$$

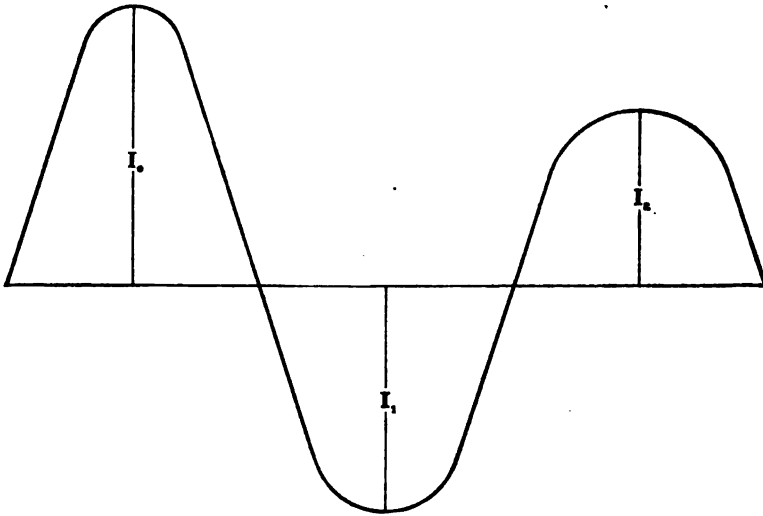


FIG. 3.—Oscillatory current with decaying amplitudes

therefore

$$2\delta = \log \left(1 + \frac{R}{Ln} \cdot e^\delta \right)$$

or

$$e^{2\delta} = 1 + \frac{R}{Ln} \cdot e^\delta$$

and

$$\frac{e^\delta - e^{-\delta}}{2} = \frac{R}{2Ln} = \delta + \frac{\delta^3}{6} + \frac{\delta^5}{120} + \dots$$

If δ is small the second and succeeding terms are negligible and we have,

$$\delta = \frac{R}{2Ln}$$

This derivation is not as exact as the first which depended upon the solution of the differential equation, since the value assumed for the mean square of the current is not exact, but approximate. This method shows the relation between the logarithmic decrement and the dissipation of energy in an interesting manner.

If undamped oscillations are induced in a circuit, as by an alternator in a primary circuit loosely coupled to this circuit, we may derive in a simple manner a method of experimentally

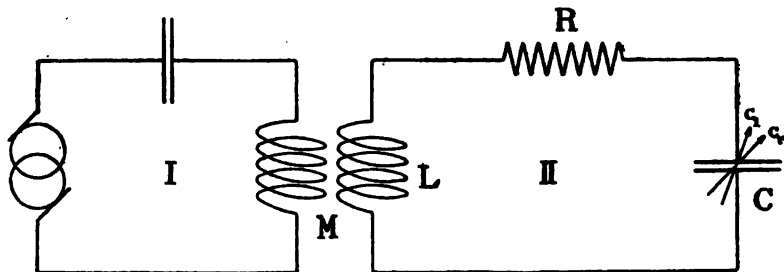


FIG. 4.—I. Exciting circuit producing undamped oscillations

II. Receiving circuit containing inductance, resistance, and variable capacity

determining the logarithmic decrement of the circuit. Circuit II in Fig. 4, which contains inductance, resistance, a variable capacity, and a current indicating device, is loosely coupled to the exciting circuit I in which there exist undamped oscillations, then at complete resonance, denoting by I_r the root mean square current,

$$(1) I_r = \frac{E}{R} \text{ and } (2) L\omega - \frac{1}{C_r\omega} = 0$$

Now, if circuit II is adjusted slightly out of resonance by changing the capacity from the resonant position C_r to another value C , then

$$(3) I = \frac{E}{\sqrt{R^2 + \left(L\omega - \frac{1}{C\omega}\right)^2}} \text{ and } (4) L\omega - \frac{1}{C\omega} = \frac{1}{C_r\omega} - \frac{1}{C\omega}$$

$\frac{1}{C_r\omega} - \frac{1}{C\omega}$ representing a very small change in reactance, therefore,

$$(5) I = \frac{E}{\sqrt{R^2 + \left(\frac{1}{C_r\omega} - \frac{1}{C\omega}\right)^2}} = \frac{E}{\sqrt{R^2 + \frac{1}{C_r^2\omega^2} \left(\frac{C_r - C}{C}\right)^2}}$$

Since

$$\delta = \pi R C_r \omega$$

$$\frac{1}{C_r\omega} = \frac{\pi R}{\delta}$$

substituting this expression in equation (5), we have,

$$(6) I = \frac{E}{\sqrt{R^2 + \frac{\pi^2 R^2}{\delta^2} \left(\frac{C_r - C}{C}\right)^2}}$$

Dividing equation (1) squared by equation (6) squared, we have

$$(7) \frac{I_r^2}{I^2} = 1 + \frac{\pi^2}{\delta^2} \left(\frac{C_r - C}{C}\right)^2$$

and from (7) we have finally

$$(8) \delta_2 = \pi \frac{C_r - C}{C} \sqrt{\frac{I^2}{I_r^2 - I^2}}$$

For the case where damped oscillations exist in both primary and secondary circuits, Bjerknes¹ has shown that the formula (8) holds good for the sum of both decrements δ_1 , and δ_2 , δ_1 being the decrement of the primary circuit and δ_2 that of the secondary circuit, or,

$$\delta_1 + \delta_2 = \pi \frac{C_r - C}{C} \sqrt{\frac{I^2}{I_r^2 - I^2}}$$

The conditions under which this formula may be applied with sufficient accuracy are,

1. That $\delta_1 + \delta_2$ be small as compared with 2π .
2. That $\frac{C_r - C}{C}$ be small as compared with unity.

¹ See V. Bjerknes "On Electrical Resonance," Wied. Ann., 55, p. 1221; 1895.

3. That the degree of coupling between the two circuits be small.

Let us assume that it is desired to determine the logarithmic decrement of the oscillations in the aerial circuit of a radio transmitter as shown in Fig. 5. A circuit containing inductance L , a calibrated variable condenser C , and a sensitive low resistance hot wire instrument H , is very loosely coupled to the aerial or antenna circuit A . Readings of the hot-wire instrument H , which

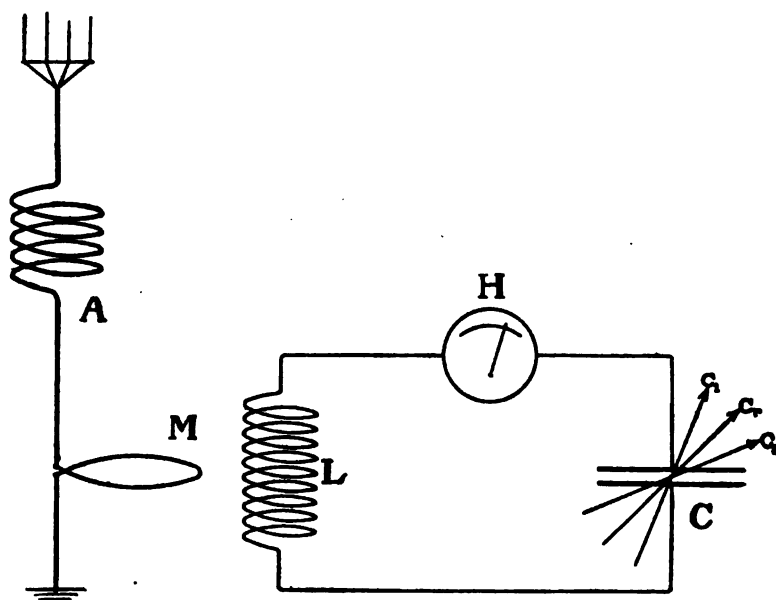


FIG. 5.—Decimeter circuit loosely coupled to the antenna circuit of a transmitter

are proportional to the square of the current in the circuit, are taken for several values of capacity C both sides of the resonant value C_r . Plotting these readings against capacity, a resonance curve as in Fig. 6 is obtained and from one of the following formulas,² the sum of the logarithmic decrements δ_1 and δ_2 may be obtained.

² In practice it is found permissible to make the change in capacity from C_r to C_1 , or from C_r to C_2 , such that L^2 becomes $\frac{1}{C^2}$, thus making the expression under the radical sign equal to unity.

$$(9) \quad \delta_1 + \delta_2 = \pi \frac{C_r - C_1}{C_1} \sqrt{\frac{I^2}{I_r^2 - I^2}}$$

$$(10) \quad \delta_1 + \delta_2 = \pi \frac{C_2 - C_r}{C_2} \sqrt{\frac{I^2}{I_r^2 - I^2}}$$

$$(11) \quad \delta_1 + \delta_2 = \pi \frac{C_2 - C_1}{C_2 + C_1} \sqrt{\frac{I^2}{I_r^2 - I^2}}$$

If the decrement δ_2 of the measuring circuit has been previously determined, the decrement δ_1 of the aerial circuit under test is at once obtained.

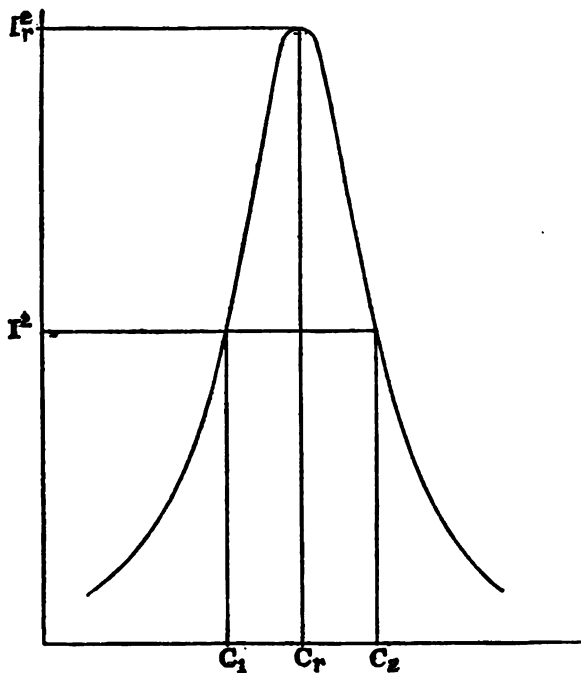


FIG. 6.—Resonance curve showing rise of current or energy in an oscillatory circuit when tuned to resonance with source of excitation

Although the measurement of the logarithmic decrement as outlined above appears to be comparatively simple, nevertheless, to obtain reasonably consistent and accurate results, the observations must be taken with considerable care, the resonance curve

must be plotted on a large scale, and calculations must be made from several points on the curve. In fact, it is only with laboratory conveniences that satisfactory measurements can be obtained.

The instrument, which it is the purpose of this paper to describe, was designed for the purpose of facilitating the work involved in making measurements of decrement and yet permitting as great

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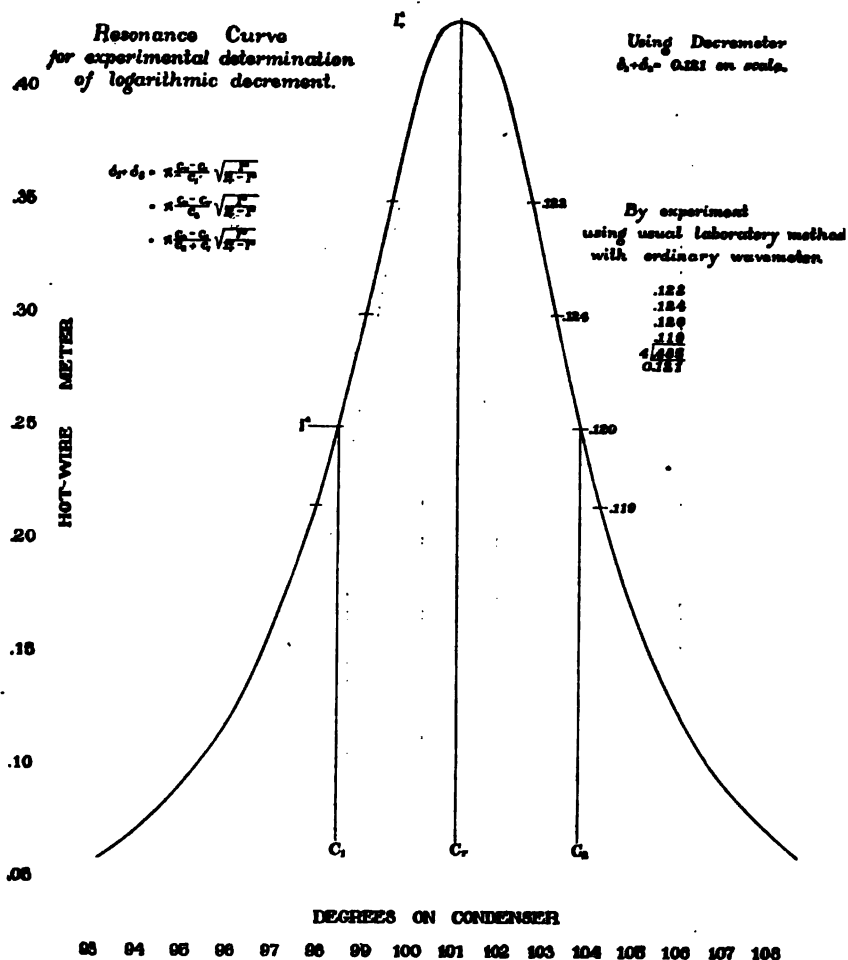


FIG. 7.—Resonance curve for experimental determination of logarithmic decrement

accuracy as can be expected in the ordinary laboratory method. These requirements are particularly desirable for the purposes of

the inspection service of the Bureau of Navigation in the enforcement of the radio communication laws. The inspection of a radio

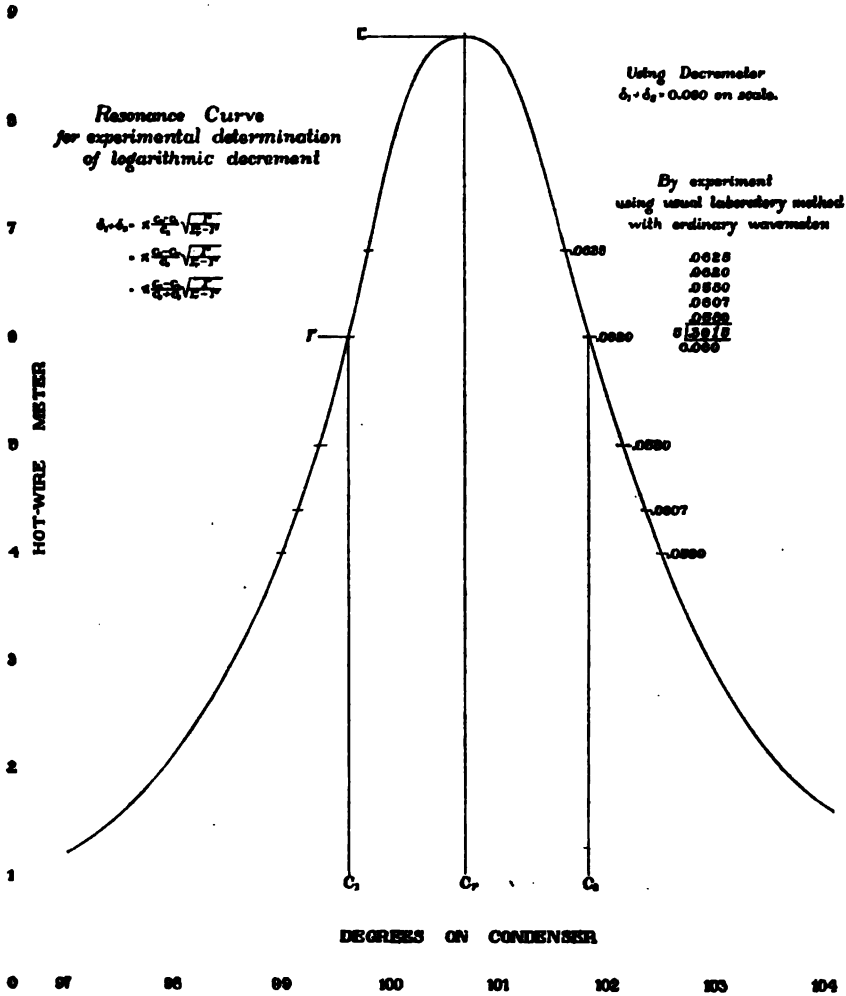


FIG. 8.—Resonance curve for experimental determination of logarithmic decrement

The above curve is plotted to a different scale from curve 7: if it were plotted to the same scale it would be twice as high and only two-fifths as broad as it is, in which case it would show better the sharper resonance.

station on board ship, for example, has to be done quickly and in many cases under very unfavorable circumstances.

In Figs. 7 and 8 typical resonance curves are shown and the task of obtaining the logarithmic decrement by the ordinary method is indicated. Identical results are obtained in a very much shorter time by means of the direct reading instrument.

3. THEORY OF THE INSTRUMENT.

The shape of the moving plates or surfaces of the ordinary variable condenser in common use is such that for equal angular displacements of these surfaces from the position of minimum capacity to that of maximum capacity, an approximately straight

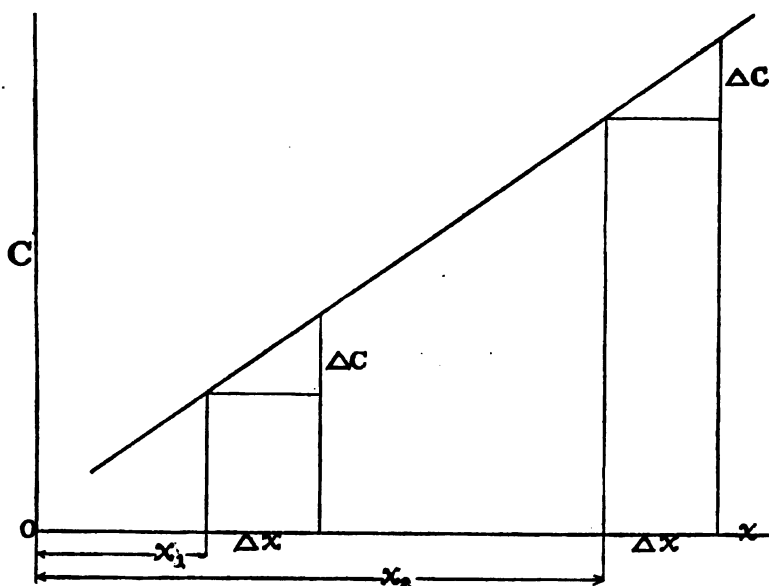


FIG. 9.—Straight line variation of capacity of the ordinary types of rotary condenser

line variation of capacity is obtained as in Fig 9. It is evident, therefore, that for any given displacement ΔX at $X = X_1$ the percentage change $\frac{\Delta C}{C}$ will not be equal to that obtained for an

equal displacement ΔX at any other point $X = X_2$.

In order to make it possible to attach to a variable condenser a single predetermined scale giving values of logarithmic decrement

corresponding to various percentage changes of capacity throughout the range of capacity of the condenser as defined by the Bjerknes formula,

$$\delta_1 + \delta_2 = \pi \frac{C_r - C}{C}, \text{ for } I^2 = \frac{1}{2} I_r^2$$

the capacity variation with equal displacements of the moving plates must be such that for any given displacement ΔX taken at any point from X minimum to X maximum,

$$\frac{C_r - C}{C} = \frac{\Delta C}{C} = \text{a constant.}$$

The problem, therefore, of constructing a direct reading instrument for decrement measurements is largely that of determining the proper shape for the plates or surfaces of the condenser to produce a variable capacity such that for any given displacement the value of $\frac{\Delta C}{C}$ will be constant throughout the range of motion of the moving surfaces.

In other words, for a displacement of ΔX , Fig. 10,

$$\frac{C_2 - C_1}{C_1} = \frac{C_3 - C_2}{C_2} = \frac{C_4 - C_3}{C_3} = \dots \dots \frac{C_n - C_{n-1}}{C_{n-1}}$$

but if,

$$\frac{C_2 - C_1}{C_1} = \frac{C_2 - C_3}{C_2}$$

then

$$C_2^2 = C_1 C_3, \text{ or } C_2 = \sqrt{C_1 C_3}$$

similarly,

$$C_3 = \sqrt{C_2 C_4}$$

or,

$$C_n = \sqrt{C_{n-1} C_{n+1}}$$

It is seen, therefore, that the capacity of the variable condenser must vary in accordance with the law of geometric progression and it is now easy to formulate the equation giving the connection between the value of capacity and the position of the moving plates,

for since the curve of capacity must obey the law of geometric progression, we have the following, Fig. 11:

$$\begin{array}{ll} \text{at } x=0 & \text{let } C_0 = aK^0 = a \\ \text{then at } x=1 & C_1 = aK^1 \\ x=2 & C_2 = aK^2 \\ x=3 & C_3 = aK^3 \\ \vdots & \vdots \\ x=n & C_n = aK^n, \end{array}$$

or, in general,

$$(12) \quad C = aK^x.$$

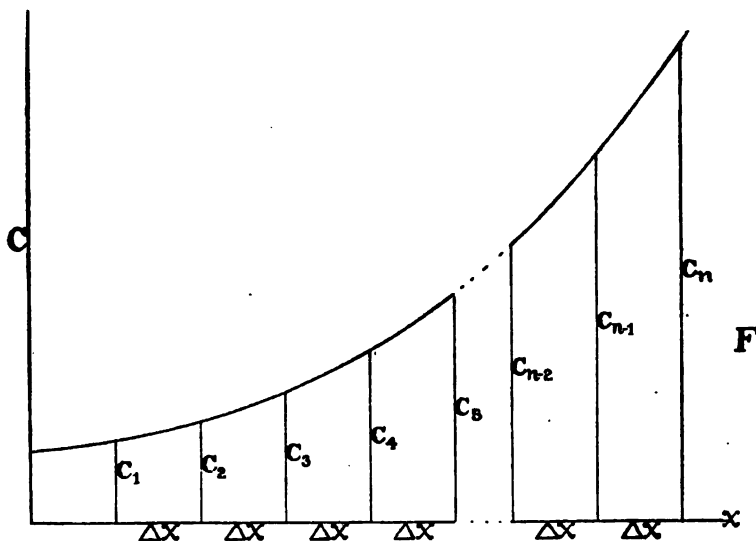


FIG. 10.—Capacity varying in accordance with the law of geometric progression

This law might have been deduced more directly as follows: The fundamental requirement of the condenser may be written:

$$(13) \quad \frac{dC}{C} = ndx$$

$$\therefore \log C = nx + h$$

and

$$C = e^{nx+h} = ae^{nx}$$

This is equivalent to equation (12). For the case of a rotary condenser where θ is the displacement angle in degrees

$$(14) \quad C = ae^{m\theta}$$

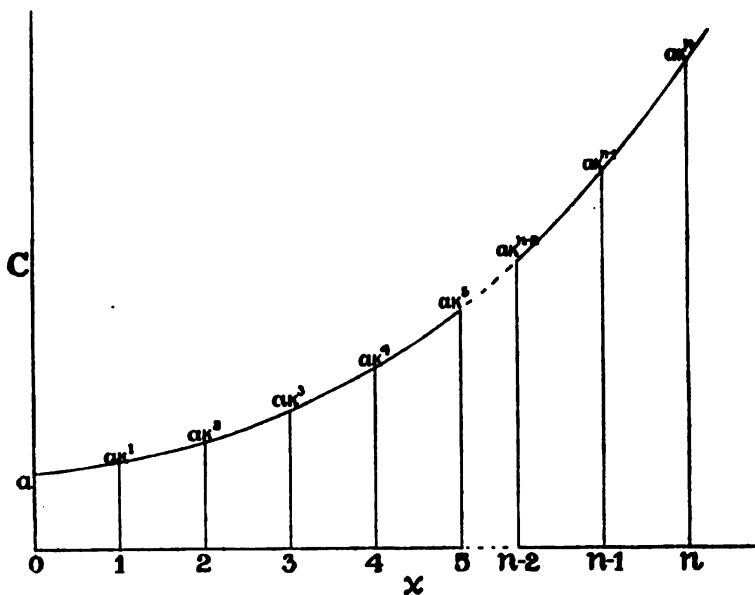


FIG. 11.—Geometric progression

4. DESIGN OF CONDENSER

Since the capacity of a condenser is directly proportional to the active area of the movable surface, neglecting edge effects we may write,

$$A = be^{m\theta}$$

A being the area of the active surface of the moving plate, and θ the angle of displacement.

If we now consider Fig. 12, the actual shape of the moving plate can be determined.

By analogy with equation 13,

$$\frac{dA}{A} = m d\theta$$

or,

$$dA = b m \epsilon^{m\theta} d\theta$$

but,

$$dA = \frac{1}{2}(\rho^2 - r^2) d\theta$$

ρ being the distance from the center O to the enveloping curve of the plate, or the radius vector, and r being the radius of the

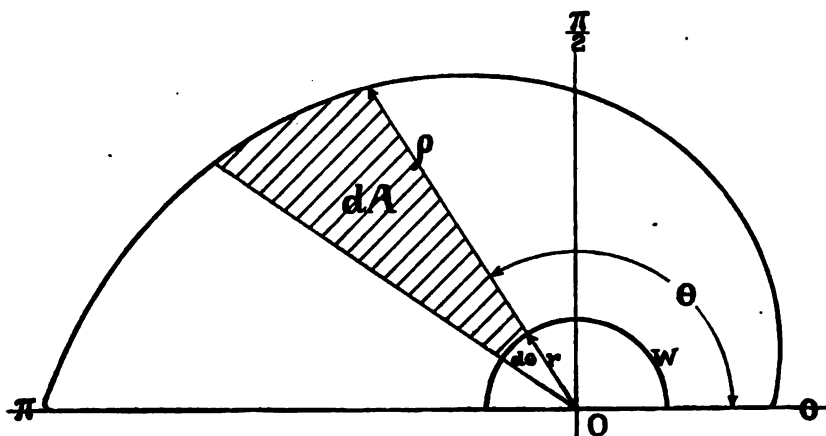


FIG. 12.—Shape of rotary plate of condenser

small circular space occupied by the separating washers between the plates.

Then

$$\frac{1}{2}\rho^2 - \frac{1}{2}r^2 = b m \epsilon^{m\theta}$$

and

$$\rho = \sqrt{2 b m \epsilon^{m\theta} + r^2}$$

b and m are constants which determine the minimum and maximum values of capacity of the condenser to be used, and having chosen these constants to suit our particular requirements, we

can immediately determine the size and shape of our plates and construct a condenser, the capacity of which will vary in accordance with the law of geometric progression.

In Fig. 13 are shown the stationary and rotary plates of the condenser. The stationary plates are made semicircular for convenience.

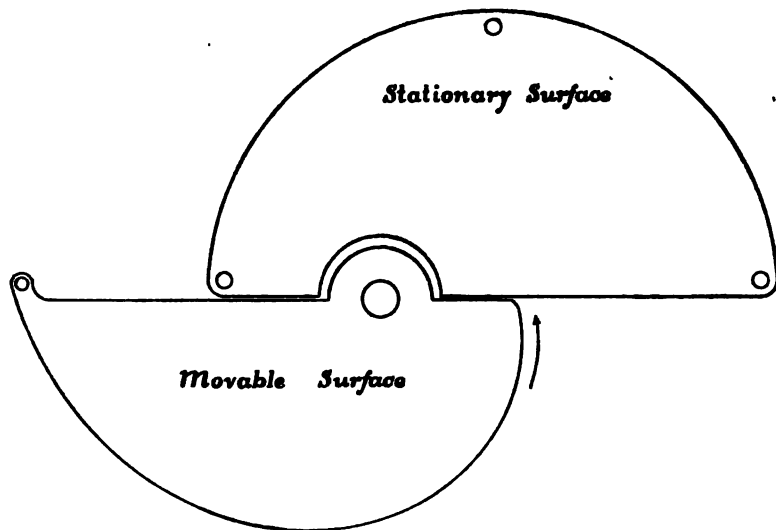


FIG. 13.—Stationary surface; movable surface

Equations 12 and 14 are identical and we may write

$$K^x = e^{m\theta}$$

or

$$x \log K = m\theta$$

therefore

$$m = \frac{x \log K}{\theta}$$

If we assume that when

$$x = 1, \theta = 180^\circ$$

then

$$x = \frac{\theta}{180}$$

and

$$m = \frac{\log K}{180}$$

therefore,

$$C = ae^{\frac{\log K}{180} \theta}$$

for

$$\theta = 0 \quad C_0 = a$$

for

$$\theta = 180^\circ \quad C_{180} = aK$$

hence, the ratio between maximum and minimum capacity will be

$$\frac{C_{180}}{C_0} = K$$

In order to obtain the ratio K which has been chosen to suit our particular requirements, a fixed condenser is connected in parallel with the rotary condenser. The capacity of this fixed condenser is determined experimentally.

A rotary condenser constructed in accordance with the theory just given, with a fixed capacity connected in parallel with it, so chosen as to give the desired ratio between the maximum and minimum capacity of the combined condensers, will give a calibration curve in exact agreement with theoretical values as shown by Fig. 14.

5. DETERMINATION OF DECREMENT SCALE

It has been shown that since the capacity of the condenser to be used in the instrument varies in accordance with the law of geometric progression, the term $\frac{C_r - C}{C}$ in the formula,

$$\delta_1 + \delta_2 = \pi \frac{C_r - C}{C} \sqrt{\frac{I^2}{I_r^2 - I^2}} = \pi \frac{C_r - C}{C}$$

when

$$I^2 = \frac{1}{2} I_r^2$$

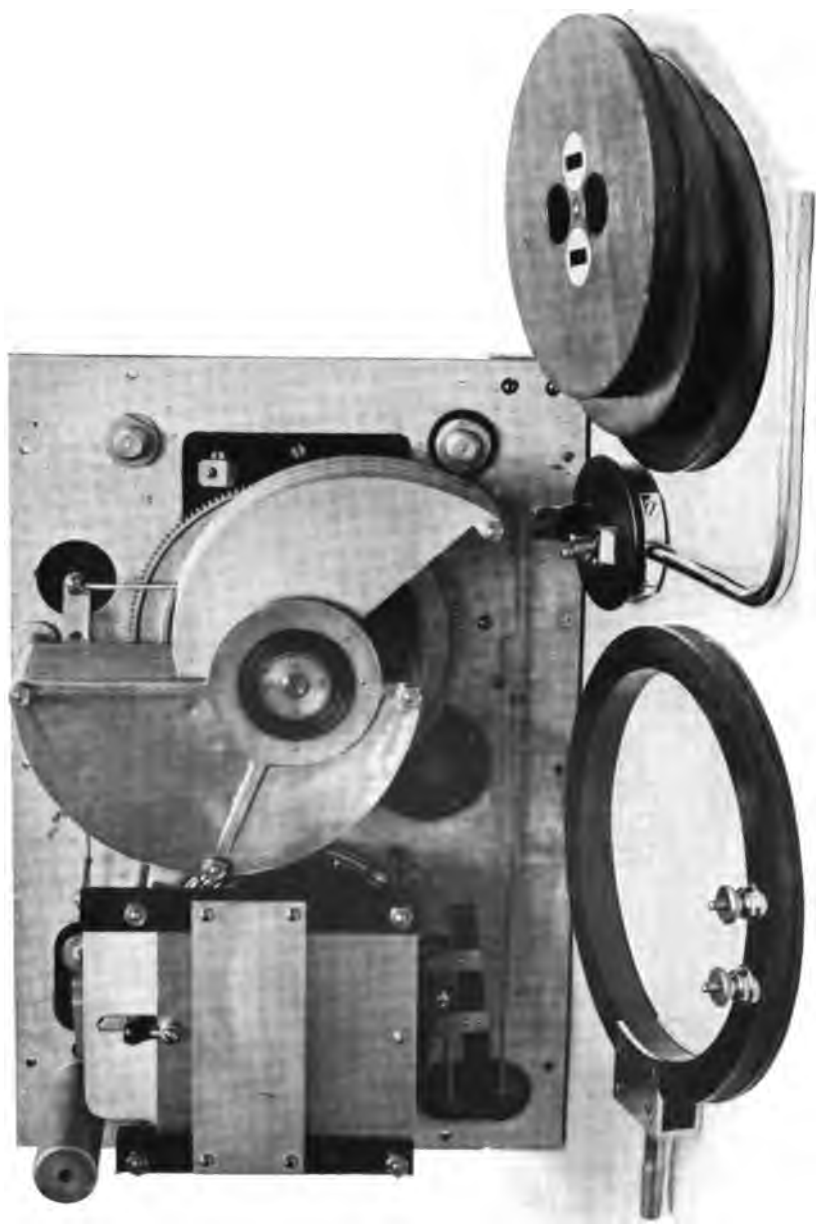


FIG. 23.—Interior view of decremeter showing condensers

will remain constant for any given angular displacement of the rotary plates throughout the range of motion from 0° to 180° .

In order, therefore, to predetermine a scale which can be attached to the rotary condenser and which will indicate directly

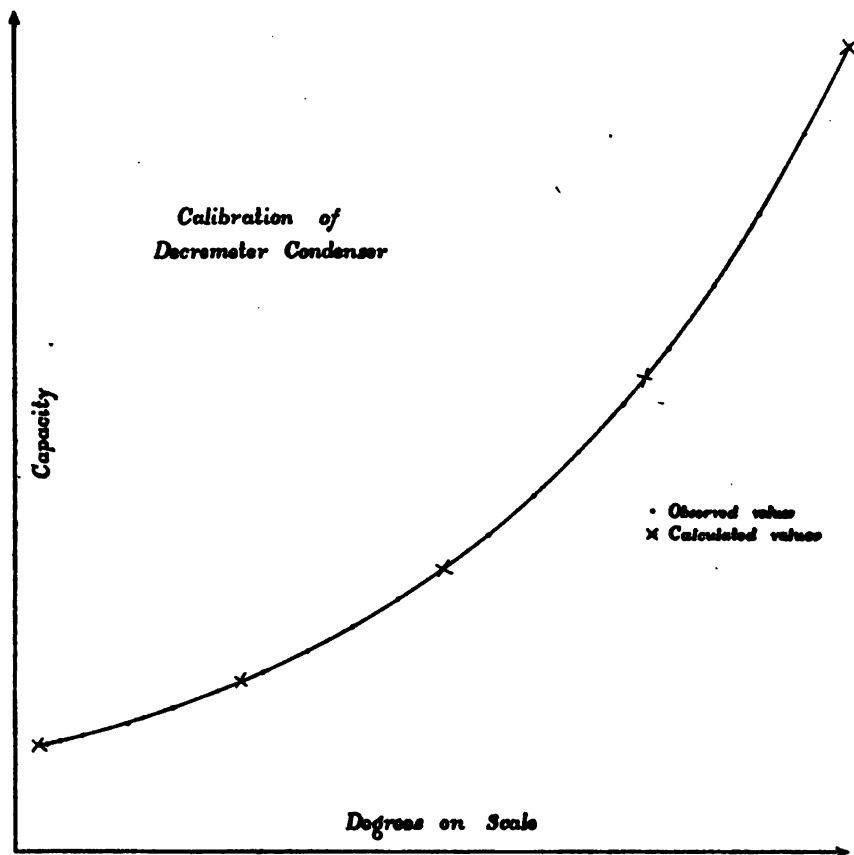


FIG. 14.—Calibration of decremeter condenser.

the value of $\delta_1 + \delta_2$ for various displacements of the rotary plates, the following calculations are made.

$$\text{Case I: } \delta_1 + \delta_2 = \pi \frac{C_r - C_1}{C_1}$$

where C_r is the value of capacity at resonance and C_1 is a smaller capacity of such a value that the current squared is reduced to one-half of its value at complete resonance.

Since C_r is proportional to $e^{m\theta_r}$ and C_1 is proportional to $e^{m\theta_1}$ we may write

$$\delta_1 + \delta_2 = \pi \frac{e^{m\theta_r} - e^{m\theta_1}}{e^{m\theta_1}} = \pi \left(e^{m(\theta_r - \theta_1)} - 1 \right)$$

let

$$\delta = \delta_1 + \delta_2 \text{ for convenience,}$$

then,

$$e^{m(\theta_r - \theta_1)} = \frac{\delta}{\pi} + 1 = \frac{\delta + \pi}{\pi}$$

and

$$\theta_r - \theta_1 = \frac{1}{m} \log \frac{\delta + \pi}{\pi}$$

The displacement angle $\Delta\theta = \theta_r - \theta_1$ may therefore be immediately calculated for various values of $\delta = \delta_1 + \delta_2$. m is as before a constant dependent upon the ratio of maximum to minimum capacity of the condenser and is equal to $\frac{\log K}{180}$, where K represents this ratio.

$$\text{Case II: } \delta_1 + \delta_2 = \pi \frac{C_2 - C_r}{C_2}$$

where C_r is again the value of capacity at complete resonance and C_2 is a larger capacity of such a value that the current squared is reduced to one-half of the value at complete resonance.

Since C_2 is proportional to $e^{m\theta_2}$ and C_r is proportional to $e^{m\theta_r}$

$$\delta = \delta_1 + \delta_2 = \pi \frac{e^{m\theta_2} - e^{m\theta_r}}{e^{m\theta_2}} = \pi \left(1 - \frac{e^{m\theta_r}}{e^{m\theta_2}} \right)$$

then

$$e^{m(\theta_2 - \theta_r)} = \frac{\pi}{\pi - \delta}$$

and

$$\theta_2 - \theta_r = \frac{1}{m} \log \frac{\pi}{\pi - \delta}$$

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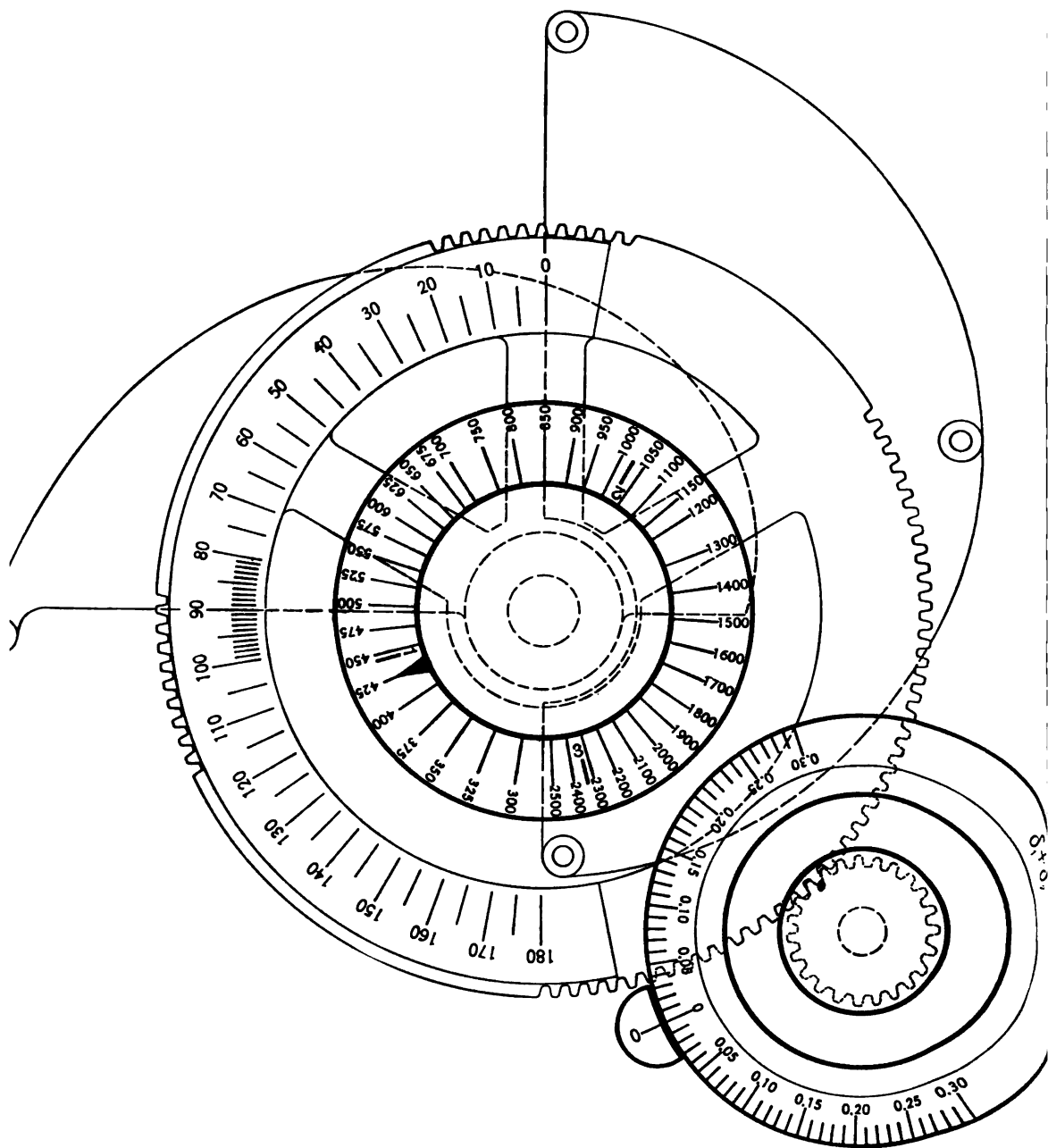


FIG. 15.—Variable condenser, showing gears and scales mechanically attached

and again, the displacement angle $\Delta\theta = \theta_2 - \theta_1$ may be readily calculated for various values of $\delta = \delta_1 + \delta_2$.

For the particular case in question, the following angles and corresponding decrements as calculated are tabulated:

$\delta_1 + \delta_2$	Case I. Reducing capacity from resonance: $\delta_1 - \delta_2$	Case II. Increasing capacity from resonance: $\delta_2 - \delta_1$
0.05	1°.292	1°.313
0.10	2°.564	2°.650
0.15	3°.821	4°.008
0.20	5°.055	5°.389
0.25	6°.272	6°.793
0.30	7°.472	8°.222

It should be emphasized that the formula

$$\delta_1 + \delta_2 = \pi \frac{C_r - C}{C} \sqrt{\frac{I^2}{I_r^2 - I^2}}$$

does not strictly apply in cases where $\delta_1 + \delta_2$ is great in comparison with 2π and $\frac{C_r - C}{C}$ is great in comparison with unity.

For $\delta_1 + \delta_2 = 0.2$ the formula may still be applied for practical purposes with reasonable accuracy. In the foregoing tabulation calculations have been made for $\delta_1 + \delta_2$ as high as 0.3, but the method and formula should preferably not be applied at values of $\delta_1 + \delta_2$ greater than 0.2.

It will be noted that the angles tabulated above are very small, and if the decrement scale were attached directly to the shaft of the condenser it would be extremely short and difficult to read.

In order to open out the scale, it is geared to the condenser shaft at a 6-to-1 ratio, as shown in Fig. 15.

Furthermore, the decrement readings are taken in such a way as to simultaneously include both measurements as defined by cases I and II. The displacement angle is then the sum of the angles tabulated under these two cases.

$$\Delta\theta = \theta_2 - \theta_r + \theta_r - \theta_1 = \theta_2 - \theta_1$$

The value of this angle $\Delta\theta = \theta_2 - \theta_1$ could have been calculated directly from the formula

$$\delta_1 + \delta_2 = \pi \frac{C_2 - C_1}{C_2 + C_1}$$

for since C_2 is proportional to $e^{m\theta_2}$ and C_1 is proportional to $e^{m\theta_1}$, then carrying out the method used in cases I and II we get directly,

$$\theta_2 - \theta_1 = \frac{1}{m} \log \frac{\pi + \delta}{\pi - \delta}$$

The final graduations for the decrement scale are obtained by multiplying $\theta_2 - \theta_1$ by the gear ratio of 6, as in the following table:

$\delta_1 + \delta_2$	$\theta_2 - \theta_1$	$(\theta_2 - \theta_1) \times 6$
0.	0	0
0.05	2°.605	15°.63
0.10	5°.214	31°.28
0.15	7°.830	46°.98
0.20	10°.444	62°.70
0.25	13°.065	78°.39
0.30	15°.694	94°.20

The decrement scale is marked to the left and to the right of zero in accordance with this table.

6. THE MEASUREMENT OF LOGARITHMIC DECREMENT

Considering now Fig. 16, the operation for measuring the logarithmic decrement is as follows:

The rotary condenser is first set at the position of complete resonance as indicated by the maximum deflection of the sensitive hot-wire instrument, the scale readings of which are proportional to the current squared. This maximum deflection is now reduced to one-half its value by decreasing or increasing the capacity of the rotary condenser. The decrement scale, which may be rotated independently, is now set at zero, then clamped so that when the condenser is again varied it will rotate with it.

Starting at the zero setting with the hot-wire instrument reading one-half the maximum deflection, the condenser is varied continu-

ously in one direction until the needle of the hot-wire instrument makes a complete excursion from one-half deflection to maximum deflection and back again to one-half deflection. The scale reading now opposite the index mark O is the value of $\delta_1 + \delta_2$, δ_1 being the

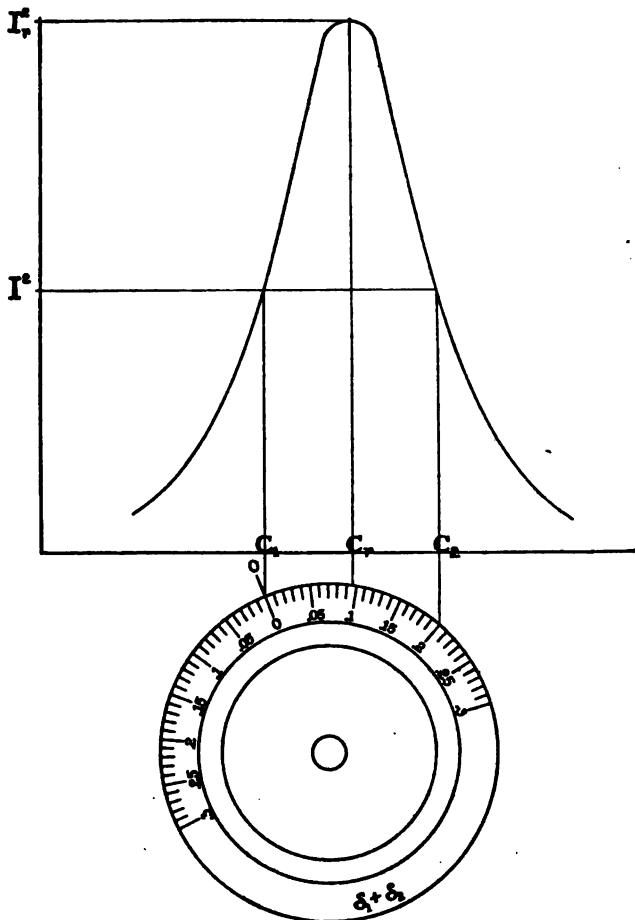


FIG. 16.—Diagram showing relation between decrement scale and resonance curve

decrement of the circuit under test and δ_2 the known decrement of the instrument.

It will be noted by referring to Fig. 16 that it is desirable to make the zero setting of the decrement scale at the point of half

deflection and also to take the final reading at the point of half deflection, because at these points the resonance curve is steep, and consequently the settings are sharply defined and easily made. In this connection it will be noted that the formula

$$\delta_1 + \delta_2 = \pi \frac{C_2 - C_1}{C_2 + C_1}$$

does not involve the resonant value of capacity, C_r , but only those at the points of half deflection where the slope of the resonance curve is steep. This formula is therefore the most desirable one

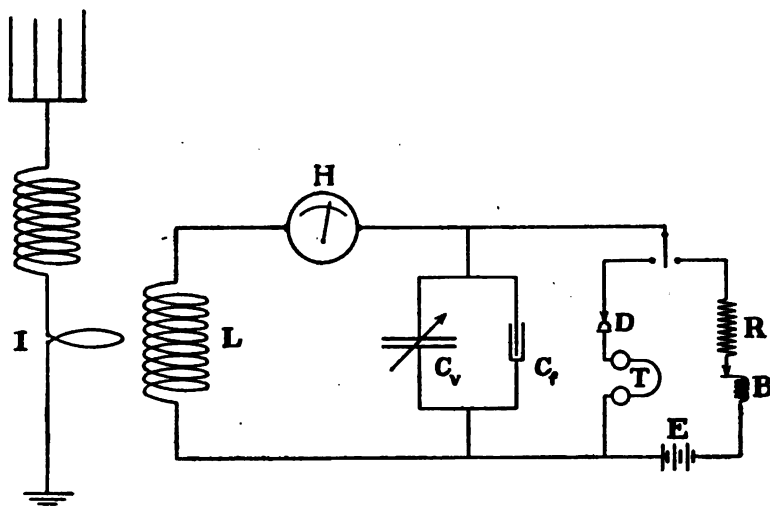


FIG. 17.—Diagram of connections

to use, and the decremeter is consequently operated in accordance with it.

In Fig. 17 a schematic diagram of the circuit is shown. I is a single-turn coil which may be connected in the circuit under test, as, for example, the aerial circuit of a radio transmitter. The inductance of this single turn is, in the majority of practical cases, small as compared with the total inductance of the circuit under test, and therefore will not affect the tuning adjustment.

The coil L is the inductance of the decremeter circuit and is so arranged that the mutual inductance between it and coil I can be



FIG. 22.—Decremeter set up for operation

easily varied. It is very essential that the degree of coupling between the circuit under test and the decrometer circuit be small.

C_v is the variable condenser to which the decrement scale is attached through gears. In parallel with C_v is a small condenser C_f which remains fixed in value after proper adjustment.

H represents the hot-wire instrument or indicating device, the scale of which is so marked that the readings are proportional to the square of the current passing through it.

A crystal detector D is provided and the wave length of distant stations may be measured by using telephone receivers T .

By means of a switch, the buzzer circuit RBE may be connected to the instrument for calibration purposes.

Fig. 18 shows a top view of the instrument in detail.

7. EXPERIMENTAL DATA

In order to determine the accuracy of the instrument for measurement of $\delta_1 + \delta_2$, the following experiments were made:

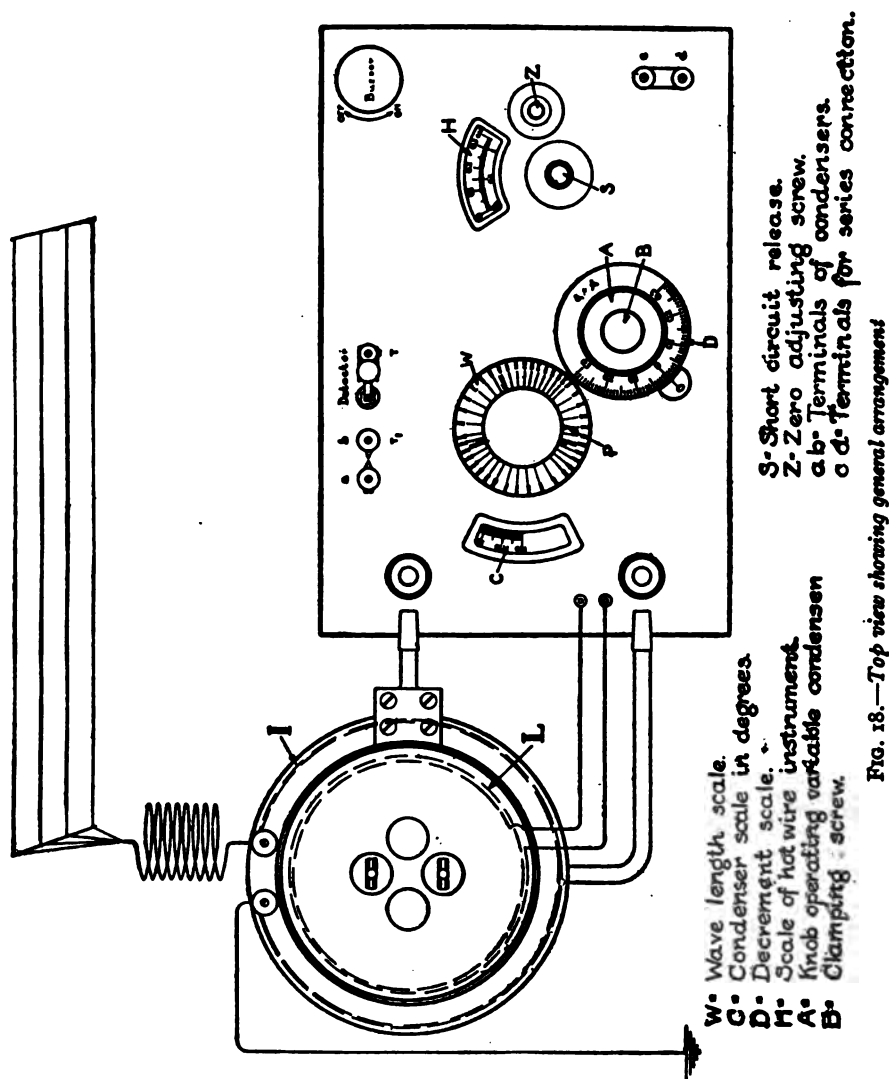
Experiment 1.—The decrometer was used as an ordinary wave meter, loosely coupled to the secondary of a quenched spark transmitter. A resonance curve was obtained similar to those shown in Figs. 7 and 8 and for several ratios $\frac{I_r^2}{I^2}$, $\delta_1 + \delta_2$ was calculated from the formula

$$\delta_1 + \delta_2 = 2\pi \frac{\lambda_2 - \lambda_1}{\lambda_2 + \lambda_1} \sqrt{\frac{I^2}{I_r^2 - I^2}}$$

and the following values obtained:

$\frac{I_r^2}{I^2}$	$\delta_1 + \delta_2$
1.180	0.0970
1.475	0.0993
1.735	0.0911
2.000	0.0903
Average	0.0919

A single measurement obtained by means of the decremeter used as a direct reading instrument gave at once a value of 0.091 for $\delta_1 + \delta_2$.



A further check was obtained by calculating the required value of $\theta_2 - \theta_1$ for $\delta_1 + \delta_2 = 0.091$ from the formula

$$\theta_2 - \theta_1 = \frac{1}{m} \log \frac{\pi + \delta}{\pi - \delta} \text{ for } P = \frac{1}{2} I,^2$$

$$\theta_2 - \theta_1 = 4^\circ.75 \text{ by calculation}$$

$\theta_2 - \theta_1 = 4^\circ.68$ as determined from the experimentally obtained resonance curve.

Experiment 2.—In this experiment the decrometer was again loosely coupled to the secondary circuit of a quenched spark transmitter and a direct measurement made of $\delta_1 + \delta_2$. A resistance, in the form of a short straight piece of about No. 40 manganin wire, was then inserted in the circuit of the instrument and a direct measurement made of $\delta_1 + \delta_2 + \Delta\delta_2$, $\Delta\delta_2$ being the additional decrement due to the inserted resistance.

The capacity of the condenser and the frequency of the oscillations being known, the value of the inserted resistance R was calculated from the formula

$$R = \frac{\Delta\delta_2}{\pi C \omega}$$

and the following results obtained.

Test No. 1

$\delta_1 + \delta_2$ read from decrement scale of instrument	$\delta_1 + \delta_2 + \Delta\delta_2$ read from decrement scale of instrument
0.132	0.168
0.130	0.169
0.130	0.163
0.131	0.172
0.130	0.167
Average=0.131	Average=0.168

$$\delta_1 + \delta_2 + \Delta\delta_2 = 0.168$$

$$\delta_1 + \delta_2 = 0.131$$

$$\therefore \Delta\delta_2 = 0.037$$

Capacity of condenser at resonance = $334\mu.\mu.f.$

$$\omega = 2\pi n = 3.66 \times 10^6.$$

$$R = \frac{\Delta\delta_2}{\pi C \omega} = 9.63\Omega$$

By measurement on D. C. bridge,

$$R = 9.51\Omega$$

Another test was made at a different frequency and consequently with a different value of capacity.

Test No. 2

$$\delta_1 + \delta_2 + \Delta\delta_2 = 0.155$$

$$\delta_1 + \delta_2 = 0.099$$

$$\Delta\delta_2 = 0.056$$

Capacity of condenser at resonance = $764\mu.\mu.f.$

$$\omega = 2\pi n = 2.47 \times 10^6$$

$$R = \frac{\Delta\delta_2}{\pi C \omega} = 9.45\Omega$$

Value of R measured on D. C. bridge = 9.51 .

$$\text{Test No. 1: } R = 9.63\Omega$$

$$\text{Test No. 2: } R = 9.45\Omega$$

$$\text{Average} = 9.54\Omega$$

Experiment 3.—In this case resistance was inserted in the secondary circuit of the transmitter and the value of this resistance calculated in the same manner as in experiment 2.

Test 1

$$\delta_1 + \Delta\delta_1 + \delta_2 = 0.141$$

$$\delta_1 + \delta_2 = 0.089$$

$$\Delta\delta_1 = 0.052$$

Capacity of condenser at resonance = $3900\mu.\mu.f.$

$$\omega = 2\pi n = 3.35 \times 10^6$$

$$R = \frac{\Delta\delta_1}{\pi C \omega} = 1.27\Omega$$

Value of R measured on D. C. bridge = 1.242Ω

Test No. 2

$$\delta_1 + \Delta\delta_1 + \delta_2 = 0.111$$

$$\delta_1 + \delta_2 = 0.074$$

$$\Delta\delta_1 = 0.037$$

Capacity of condenser at resonance = $3900\mu.\mu.f.$

$$\omega = 2.43 \times 10^6$$

$$R = \frac{\Delta\delta_1}{\pi C \omega} = 1.24\Omega$$

Test No. 1: $R = 1.27\Omega$

Test No. 2: $R = 1.24\Omega$

Average = 1.255Ω

8. DETERMINATION OF WAVE-LENGTH SCALE

Since the capacity of the variable condenser in the instrument varies according to a definitely known law, it is possible to attach to this condenser a predetermined scale indicating wave lengths directly. The graduations of the wave length scale are determined by calculation in the following manner:

It has been shown that the capacity of the condenser may be expressed as $C = ae^{m\theta}$.

The wave length λ is proportional to $\sqrt{C}$

therefore, λ is proportional to $\sqrt{e^{m\theta}}$

or λ is proportional to $e^{\frac{m\theta}{2}} = e^{n\theta}$

where

$$n = \frac{m}{2}$$

Now let λ_1 be any wave length within the range of the instrument, and λ_2 any other wave length desired, then

$$\frac{\lambda_2}{\lambda_1} = \frac{e^{n\theta_2}}{e^{n\theta_1}} = e^{n(\theta_2 - \theta_1)}$$

and

$$\log \frac{\lambda_2}{\lambda_1} = n(\theta_2 - \theta_1)$$

or

$$\theta_2 - \theta_1 = \frac{1}{n} \log \frac{\lambda_2}{\lambda_1} = \frac{2}{m} \log \frac{\lambda_2}{\lambda_1}$$

therefore

$$\theta_2 = \theta_1 \pm \frac{2}{m} \log \frac{\lambda_2}{\lambda_1}$$

For the purpose of determining the graduations for the scale, λ_1 may be any wave length, as, for example, 300 meters. Furthermore, θ_1 may be taken as zero, for convenience, then

$$\theta_2 = \pm \frac{2}{m} \log \frac{\lambda_2}{300}$$

From this equation θ_2 may be calculated for any wave length λ_2 . The scale will appear as shown in Fig. 19.

The scale is arranged so that it can rotate about the shaft of the variable condenser independently but remains stationary when the condenser is rotated. A pointer is attached to the shaft of the condenser and travels over the scale as the condenser rotates.

In order to cover a wide range of wave lengths, several coils are supplied with the instrument, each coil covering a part of the range. It is necessary, therefore, to adjust the position of the wave length scale to correspond with the particular coil in circuit. The red marks shown in Fig. 19 indicate the maximum wave length obtainable with the coils 1, 2, and 3, respectively. The position of these red marks is determined experimentally.

9. THE MEASUREMENT OF WAVE LENGTH

The variable condenser is first set at 180°, the wave length scale is then adjusted so that the red mark on the scale corresponding to the coil in circuit is directly under the pointer attached to the

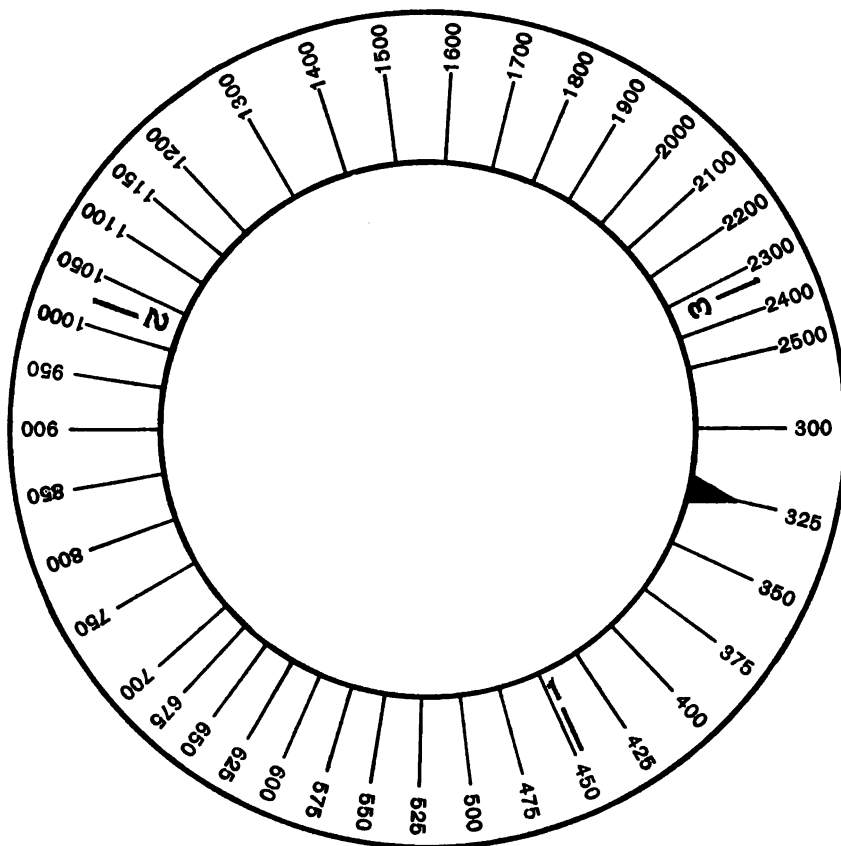


FIG. 19.—Wave-length scale

condenser shaft. The wave length scale remains in this position and, as the condenser is varied, the pointer travels over the scale, indicating the wave length when resonance is obtained, as shown by the maximum reading of the hot wire instrument needle.

When the instrument is used as a receiver with detector and telephones, or as a transmitter using the buzzer, the wave length scale does not strictly apply for the wave length range below the 90° position of the condenser. In these cases it is necessary to refer to calibration curves for the small correction.

The instrument may be used in an interesting manner for receiving audible signals from a source of undamped oscillations, such as an arc circuit or a high frequency alternator. To accomplish this, oscillations are set up in the wave meter circuit by means of the buzzer and the telephone receivers are connected to the detector at *T* and to the binding post *a* instead of *b*, see figure 18. Under these conditions, when undamped oscillations are induced in the circuit, a heterodyne effect is produced and the wave meter becomes a comparatively sensitive receiver of undamped oscillations. Very weak harmonics existing in arc circuits may be readily measured by using the instrument in this manner.

10. DETERMINATION OF THE DECREMENT OF THE INSTRUMENT

To obtain the logarithmic decrement, δ_1 , of the circuit under test, it is necessary to know δ_2 , the decrement of the instrument, in order that it may be subtracted from the scale reading which is $\delta_1 + \delta_2$.

An ideal method for determining δ_2 would be to charge the condenser of the instrument at a given potential and allow it to discharge through the circuit, first without inserted resistance and then with a known resistance inserted in the circuit, noting in each case the reading of the hot wire instrument.

The energy in the circuit in both cases would then be equal and,

$$I_1^2 R = I_2^2 (R + \Delta R)$$

where *R* is the resistance of the circuit and ΔR is the resistance inserted. Then,

$$R = \Delta R \frac{I_2^2}{I_1^2 - I_2^2}$$

where I_2^2 and I_1^2 represent, respectively, the readings of the hot wire instrument with and without inserted resistance, these readings being proportional to the square of the current flowing in the circuit.

If the inductance L or capacity C of the circuit are known, δ_2 is then determined for any value of ω , since,

$$\delta_2 = \pi RC\omega = \pi \frac{R}{L\omega}$$

A method used in practice which approaches this ideal case very closely is as follows:

Energy is supplied to the instrument by means of impact excitation, in which case nearly free oscillations exist in the circuit of the instrument. These oscillations, therefore, have a frequency and damping determined by the constants of the circuit. To determine the resistance of the circuit, readings of the hot wire instrument are taken with and without inserted resistance. The energy in the circuit, however, would not in practice be strictly equal in the two cases and

$$I_1^2 R = K I_2^2 (R + \Delta R)$$

or

$$R = \Delta R \frac{K I_2^2}{I_1^2 - K I_2^2}$$

It has been shown in previous works³ on this subject that

$$K = 1 + \frac{\Delta\delta}{\delta_1 + \delta_2}$$

Where δ_1 is the decrement of the exciting circuit, δ_2 the decrement of the instrument circuit, and $\Delta\delta$ the additional decrement due to the insertion of a small resistance ΔR .

It is seen that for the case of impact excitation where δ_1 is very large as compared to $\Delta\delta$, K will be very nearly unity and for practical purposes we may write

$$R = \Delta R \frac{I_2^2}{I_1^2 - I_2^2} = \Delta R \frac{1}{\frac{I_1^2}{I_2^2} - 1}$$

³Lehrbuch der Drahtlosen Telegraphie. Zenneck, 1913, p. 142.

Where it is desired to make ΔR , the inserted resistance equal to R , the resistance of the instrument circuit, which corresponds to making $\Delta\delta$ equal to δ_1 , then for the case of impact excitation,

$$\frac{I_1^2}{I_2^2} = 2$$

On the other hand, if $\delta_1 = 0$ as in the case of undamped oscillations,

$$K = 2 \text{ and } \frac{I_1^2}{I_2^2} = 4$$

In general, therefore, when it is desired to make the inserted resistance ΔR equal to the resistance of the instrument R , the amount by which I_1^2 must be reduced or the ratio of $\frac{I_1^2}{I_2^2}$ depends upon the ratio of δ_1 to δ_2 for when $\Delta\delta = \delta_2$,

$$K = 1 + \frac{\delta_2}{\delta_1 + \delta_2} = 1 + \frac{1}{\frac{\delta_1}{\delta_2} + 1}$$

and for

$$\delta_1 = 0 \quad K = 2 \text{ and } \frac{I_1^2}{I_2^2} = 4$$

$$\delta_1 = \infty \quad K = 1 \text{ and } \frac{I_1^2}{I_2^2} = 2$$

For intermediate values of $\frac{\delta_1}{\delta_2}$ between 0 and ∞ , K will vary from 2 to 1 and the ratio $\frac{I_1^2}{I_2^2}$ correspondingly from 4 to 2.

The most direct and simple method, however, for obtaining δ_2 is to excite the instrument by means of undamped oscillations, then

$$\delta_2 = \pi \frac{C_2 - C_1}{C_2 + C_1} \sqrt{\frac{I^2}{I_r^2 - I^2}}$$

as shown in the earlier part of this paper.

If suitable means for producing undamped oscillation are not available the method of impact excitation is very satisfactory; provided that δ_1 is very large as compared with $\angle\delta$.

The curves in Fig. 20 give the values of δ_2 for coils 1, 2, and 3,

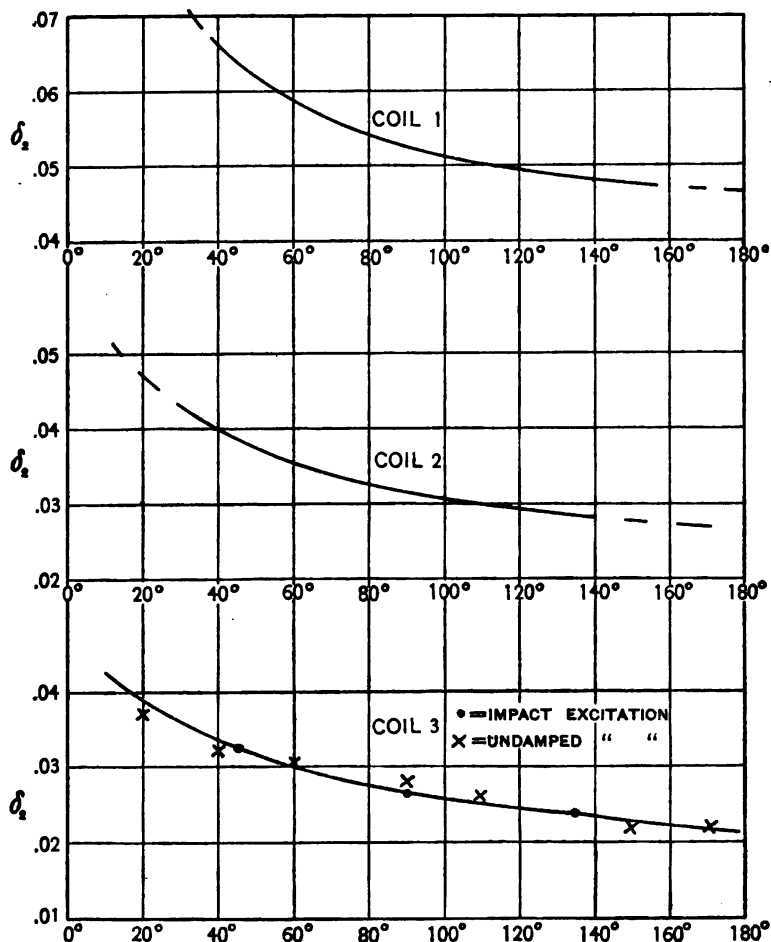


FIG. 20.—Decrement of instrument

at various settings of the variable condenser. These values were obtained by the method of impact excitation.

On curve 3 are shown values of δ_2 obtained by using undamped oscillations from a Poulsen arc as a source of excitation.



FIG. 21.—Decrometer mounted in leather carrying case

In conclusion, I wish to take this opportunity to express my thanks to Mr. E. T. Chamberlain, Commissioner of Navigation, and to Dr. E. B. Rosa, Chief Physicist of the Bureau of Standards, for the keen interest they have taken in the development of the decremeter and for their helpful encouragement which they have given me from time to time.

WASHINGTON, August 15, 1914.

82780°—15—9

ELECTRICAL RESISTANCE AND CRITICAL RANGES OF PURE IRON

By G. K. Burgess and I. N. Kellberg

The exact location and description of the critical ranges A₂ and A₃ of pure iron, determined by heating and cooling curves, has recently been published by the Bureau of Standards.¹ Dr. Benedicks, of Stockholm, has since carried out dilatation measurements² which show that A₂ is accompanied by an expansion change hitherto undetected. Messrs. Honda and Ogura,³ following a number of other experimenters,⁴ have plotted the magnetic and resistance-temperature curves for pure iron over the range 0° to 1000° C. Although their observations appear to give the general trend of the resistance-temperature curve of pure iron, they do not give an exact representation of the resistance changes taking place at A₂ and A₃, mainly for lack of sensitiveness.

In view of the importance of the subject and as providing a part of an adequate experimental basis for the elucidation of the question of the allotropy of iron it was thought worth while to make as exact a determination of the resistance-temperature relation of pure iron as the experimental means at our command permitted, paying particular attention to the form of the curve over the A₂ and A₃ critical ranges.

The experiments here described were begun in the summer of 1912, and several preliminary methods of experimentation were tried out before satisfactory sensitiveness, accuracy, speed in

¹ G. K. Burgess and J. J. Crowe: Critical Ranges A₂ and A₃ of Pure Iron, Scientific Paper No. 213, 1914; also Bull. Am. Inst. Mining Engineers, No. 82, Oct. 1913, p. 2537, and discussion, *ibid.*, Dec. 1913.

² Carl Benedicks: Experiments on allotropy of iron; Behavior of ferro-magnetic mixtures; Dilatation of pure iron; J. Iron and Steel Institute, May, 1914.

³ K. Honda und Y. Ogura: Über die Beziehung zwischen den Änderungen der Magnetisierung und des Elektrischen Widerstandes im Eisen, Stahl und Nickel bei hohen Temperaturen, Science Reports, University Sendai, 8, p. 113, 1914.

⁴ See Bureau of Standards Scientific Paper No. 213, above cited.

manipulation, and closeness of observations to each other were obtained. In some of the earlier work the method was tried of bringing the heating bath or furnace to a definite temperature and waiting for equilibrium to be established. It soon became evident that, although great sensitiveness and accuracy could be obtained, nevertheless it would take an infinite time to plot the entire resistance-temperature curve satisfactorily. The method adopted in the final series, and which satisfies all the above requirements, depends on the use of the cooling curve apparatus described in Scientific Paper No. 213 (*loc. cit.*), together with a very sensitive, quickly manipulated, and accurate Wheatstone bridge, by means of which latter the resistances of an iron wire and one of platinum wound on the same support and inclosed in

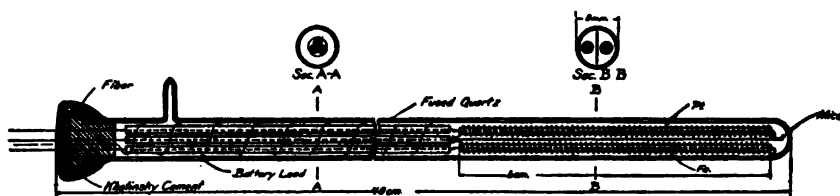


FIG. 1.—Construction of platinum and iron thermometers

vacuo in quartz glass may be exactly compared every few seconds by the intermediary of a drum chronograph recording the times at which the resistances are measured; or, in other words, we have used an electrical resistance cooling curve outfit of the highest attainable accuracy and sensitiveness. The temperatures are given in terms of the resistance of the platinum wire, which serves as a thermometer integrating the temperature of the iron wire exactly.

The construction of the combined platinum and iron thermometers is shown in Fig. 1. The platinum and iron wires of 0.2 mm and 0.24 mm diameter, respectively, are wound on thin-walled, unglazed, hard porcelain insulators 6 cm in length and separated by a strip of mica. The thermometers are of the compensated three-lead type, with one common lead and a common battery lead, all four leads being of platinum and provided with porcelain insulators. After winding the coils and before sealing off, the

quartz containing tube was evacuated and, with the coils, heated to a bright red, thus partly annealing the wires and expelling gases. After sealing, the thermometers were again annealed to about 1000°C in the electric furnace. Several platinum and iron thermometers were made in this way, the values of the resistances at 0°C usually being about 1.5 ohms for the platinum and 1 ohm for the iron. The length of the thermometer was about 0.1 that of the specially wound platinum resistance furnace used in taking the resistance observations. The iron was from samples of the purest described in Scientific Paper No. 213 (99.98 per cent iron). The design of the furnace and heating circuits were such that the rate of heating could be exactly controlled and the temperature of the iron was constant over its length at any instant. The Wheatstone bridge with which the best series were taken is one designed by E. F. Mueller, of this Bureau, it being a modification of the one described in Bureau of Standards Reprint 124, in which are also described the methods of use of the resistance pyrometer. The precision of the resistance measurements was better than 0.00001 ohm and of the time 0.1 sec., or equivalent to 0.005°C in temperature differences and to 1 in 1 000 000 of the iron resistance at 800°C . This is some 1000 times the precision of Honda and Ogura.

In all, six iron thermometers were used from three samples, and all gave the same characteristics for pure iron. In Fig. 2 are shown the observations of the second heating and cooling curves taken with thermometer F-6, which are typical of the behavior of iron, and in Fig. 3 the temperature coefficient of electrical resistance of pure iron, or more exactly the ratio of change of resistance of iron to that of platinum with temperature. In Tables 1, 2, and 3 are given the actual observations from which these curves are drawn, except that the lower region of the curve of Fig. 3 is plotted from numerous observations on several iron samples.

In Fig. 2 the observations on heating are represented by circles and on cooling by crosses. The shift of the heating curve with respect to the cooling curve appears to be real, as shown, since the iron returns exactly to the same resistance at 0°C after heating. This noncoincidence of heating and cooling curves is probably

caused by the different rates of heating and cooling, the former being about 0.10 deg./sec. and the latter 0.06 deg./sec. at 900° C.

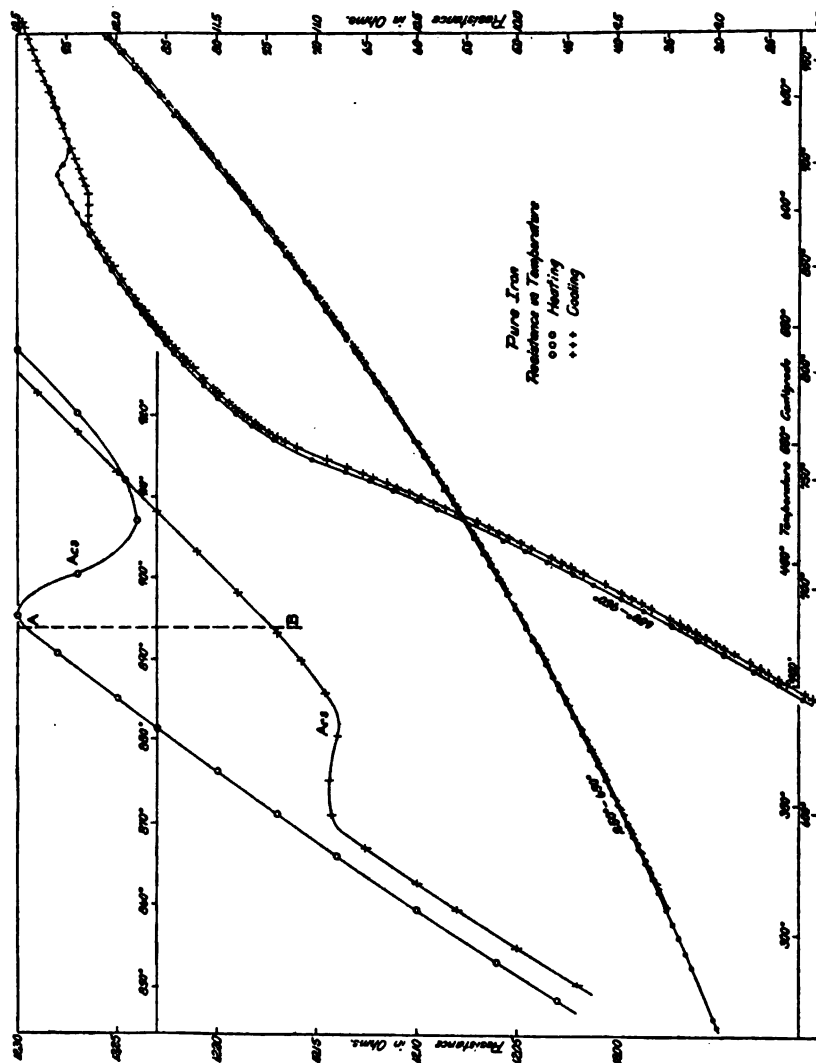


FIG. 2.—Resistance—Temperature curve of pure iron

It is seen from Figs. 2 and 3 that the resistance of iron increases from 0° C without any anomalies except possibly a minute one at 730° C due to less than 0.01 per cent of carbon, with a gradually

increasing temperature coefficient to above 650° or until the neighborhood of A_2 is reached. As A_2 is approached the resistance rises rapidly, and at A_2 there is an inflexion in the resistance-temperature curve shown as a cusp at 757° C in the temperature coefficient curve. At A_{c3} the resistance of iron falls abruptly by some 0.005 of its value, which is recovered within a 25° interval, and above A_{c3} increases gradually again. On cooling, the reverse phenomenon is observed at A_{r3} , which is accompanied by a slight increase in resistance with falling temperature, preceded by an

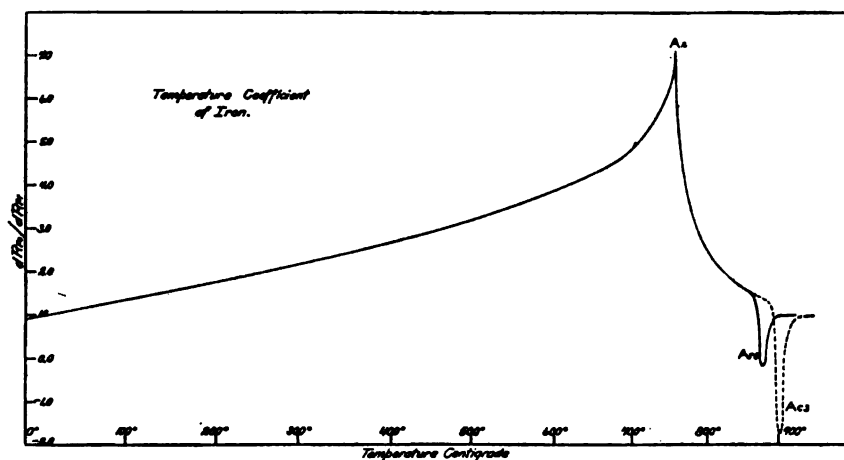


FIG. 3.—Temperature—Coefficient of pure iron

interval of relatively slight changes in resistance. These effects are shown best in the open scale plot in Fig. 2 of the A_3 region and in Fig. 3.

As closely as can be measured, the transformations A_{c3} and A_{r3} begin at the same temperature, 894° C (see line AB of Fig. 2); and, as given by the resistance measurements, A_{c3} and A_{r3} each extend over the considerable temperature interval of 25° C.

These resistance measurements therefore show that A_2 is a strictly reversible transformation and that A_3 is a transformation taking place at a higher temperature on heating than on cooling. Evidently the two types of transformation are fundamentally different.

The experiments here described are in agreement with the thermal observations previously recorded (see Scientific Paper No. 213), although the position of maximum absorption or evolution of heat does not appear to coincide exactly with the temperatures at which the electrical resistance is changing most rapidly either at A₂ or A₃. The type of phenomenon is, however, the same as given by either method for A₂ and A₃, respectively.

Whether or not either or both of these critical ranges, A₂ and A₃, are to be considered an "allotropic point" will depend on the definition of allotropy, about which there does not yet appear to be agreement. The reversible thermal and electrical behavior at A₂ appears to be somewhat similar to that of a pure substance at its melting point, while at A₃ there is a progressive change with temperature of the electrical and thermal properties which are not reversible, the reaction taking place at a higher temperature on heating than on cooling. The A₃ change is certainly associated with recrystallization, while no crystallographic change has as yet been found at A₂, which is also the temperature associated with the abrupt, reversible change of iron from the ferro-magnetic to the para-magnetic states.

WASHINGTON, August 21, 1914.

TABLE 1
Second Heating of F-6

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms ^a	secs.	ohms ^a	secs.	ohms
2.76	135.3	2.84	69.8	2.76658
2.77	29.3	2.85	128.5	2.77184
2.78	29.7	2.87	107.3	2.78217
2.79	25.2	2.89	85.2	2.79229
2.80	29.3	2.91	14.0	2.80676
2.81	29.1	2.93	68.0	2.81300
2.82	86.3	2.95	60.2	2.82589
2.83	68.0	2.96	92.0	2.83850
2.85	61.7	3.01	81.0	2.85867
2.87	23.8	3.05	43.7	2.87353
^a 2.88				
2.96	29.8	3.26	26.2	2.97396

^a Resistances are actually read to 0.00001 ohms; thus, for 2.76 read 2.76000, etc.

^b Increased current in furnace from 3.5 amperes to 5.0 amperes.

TABLE 1—Continued
Second Heating of F-6—Continued

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
2.99	22.3	3.32	27.6	3.00340
3.02	25.5	3.39	22.6	3.03591
3.05	20.6	3.45	25.3	3.06346
3.08	16.0	3.51	29.0	3.09066
3.11	24.1	3.59	19.7	3.12650
3.14	19.3	3.65	24.1	3.15344
3.17	19.9	3.72	22.5	3.18408
3.20	20.2	3.79	22.9	3.21406
3.23	12.4	3.85	14.0	3.23939
3.25	15.4	3.90	26.0	3.26116
3.28	19.5	3.98	21.0	3.29444
3.31	18.0	4.05	22.1	3.32347
3.34	15.9	4.12	24.2	3.35189
3.37	13.2	4.19	26.0	3.38009
3.40	16.0	4.27	23.2	3.41225
3.43	17.2	4.35	21.4	3.44336
3.46	23.7	4.44	14.8	3.47845
3.49	19.7	4.51	18.5	3.50548
3.52	15.0	4.58	22.0	3.53216
3.55	9.6	4.65	15.3	3.55771
3.57	13.0	4.71	24.8	3.58032
3.60	12.4	4.79	13.6	3.60953
3.62	14.0	4.85	10.0	3.63136
3.64	17.2	4.91	33.8	3.65350
3.68	15.1	5.02	21.6	3.69234
3.71	13.2	5.10	24.2	3.72050
3.74	15.2	5.19	22.0	3.75226
3.77	12.0	5.27	12.4	3.77983
3.79	17.0	5.34	20.2	3.80372
3.82	17.2	5.43	20.0	3.83367
3.85	30.2	5.55	19.7	3.87420
3.89	16.3	5.64	20.7	3.90321
3.92	14.8	5.73	22.3	3.93196
3.95	17.6	5.83	19.1	3.96438
3.98	20.4	5.93	17.0	3.99638
4.01	22.5	6.03	16.6	4.02726
4.04	14.4	6.11	22.2	4.05180
4.07	19.3	6.22	17.9	4.08556
4.10	13.2	6.30	25.2	4.11031
4.13	20.5	6.42	18.1	4.14592
4.16	16.0	6.51	22.6	4.17242
4.19	19.3	6.62	19.8	4.20480
4.22	13.8	6.71	25.1	4.23064
4.25	15.6	6.82	23.7	4.26191
4.28	12.8	6.92	13.6	4.28701
4.30	18.8	7.00	23.3	4.31212
4.33	20.9	7.12	18.6	4.34596

TABLE 1—Continued
Second Heating of F-6—Continued

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
4.36	17.3	7.22	23.0	4.37287
4.39	12.7	7.32	15.0	4.39673
4.41	17.8	7.41	21.5	4.42359
4.44	13.3	7.51	27.8	4.44970
4.47	18.2	7.64	22.8	4.48331
4.50	16.2	7.75	25.3	4.51172
4.53	19.8	7.88	21.8	4.54428
4.56	20.4	8.00	22.5	4.57426
4.59	30.9	8.15	25.0	4.61219
4.63	36.0	8.33	21.5	4.65510
4.67	12.4	8.43	31.4	4.67859
4.70	20.8	8.58	23.8	4.71400
4.73	17.3	8.70	27.0	4.74171
4.76	14.0	8.82	31.8	4.76916
4.79	19.2	8.97	26.4	4.80291
4.82	17.8	9.10	28.4	4.83156
4.85	15.3	9.23	31.5	4.85980
4.88	15.3	9.37	17.8	4.88924
4.90	20.7	9.48	21.3	4.91479
4.93	19.2	9.62	13.4	4.94178
4.95	19.3	9.72	28.8	4.96204
4.98	12.3	9.85	20.8	4.98742
5.00	15.0	9.96	18.4	5.00898
5.02	16.0	10.07	33.0	5.02980
5.05	17.3	10.20	32.4	5.06043
5.08	19.1	10.40	15.0	5.09120
5.10	14.2	10.50	19.6	5.10846
5.12	15.2	10.62	19.8	5.12863
5.14	13.6	10.74	19.8	5.14814
5.16	11.6	10.86	23.2	5.16666
5.18	19.5	11.03	17.4	5.19055
5.20	50.2	11.22	36.0	5.22913
5.25	14.9	11.33	22.2	5.25803
5.27	21.9	11.41	34.3	5.28169
5.30	23.5	11.50	30.5	5.31306
5.33	18.8	11.57	19.8	5.33974
5.35	18.6	11.62	19.3	5.35982
5.37	20.6	11.67	18.0	5.38067
5.39	24.8	11.72	14.6	5.40259
5.41	21.6	11.76	16.7	5.42128
5.43	22.1	11.80	17.5	5.44116
5.45	22.7	11.84	17.6	5.46126
5.47	25.3	11.88	15.0	5.48256
5.49	18.0	11.91	23.2	5.49874
5.51	22.9	11.95	18.2	5.52114
5.53	29.6	11.99	34.1	5.54394
5.56	16.6	12.03	25.2	5.56794
5.58	15.1	12.06	28.1	5.58683

TABLE 1—Continued
Second Heating of F-6—Continued

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
5.60	27.1	12.10	38.9	5.61232
5.63	19.6	12.14	23.2	5.63915
5.65	22.3	12.17	21.8	5.66011
5.67	25.3	12.20	17.5	5.68182
5.69	29.6	12.23	15.6	5.70310
5.71	18.5	12.25	26.5	5.71822
5.73	25.5	12.28	21.6	5.74083
5.75	22.0	12.30	23.1	5.75974
5.77	29.5	12.27	19.3	5.78029
5.79	41.0	12.24	30.2	5.80727
5.82	18.2	12.246	21.6	5.82728
5.836	60.8	12.27	46.4	5.86090
5.88	31.1	12.30	20.2	5.89213
5.90	33.6	12.32	17.6	5.91310
5.92	34.6	12.34	15.7	5.93376
5.94				

TABLE 2
Second Cooling of F-6

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
6.08	32.8	12.49	22.5	6.07408
6.07	40.0	12.47	14.6	6.06372
6.06	43.7	12.46	66.5	6.05208
6.04	52.3	12.44	51.7	6.02994
6.02	58.2	12.42	40.8	6.00825
6.00	61.0	12.40	36.5	5.98749
5.98	63.6	12.38	28.0	5.96611
5.96	67.1	12.36	24.5	5.94535
5.94	24.8	12.35	21.1	5.93460
5.93	27.0	12.34	18.2	5.92403
5.92	28.7	12.33	15.8	5.91355
5.91	30.0	12.32	14.3	5.90322
5.90	31.8	12.31	56.2	5.89278
5.88	38.3	12.29	46.6	5.87100
5.86	35.0	12.27	49.2	5.85167
5.84	35.4	12.25	48.0	5.83152
5.82	36.2	12.23	30.2	5.81183
5.805	52.8	12.21	47.0	5.79180
5.78	37.2	12.19	46.7	5.77112
5.76	36.7	12.17	25.8	5.75119

TABLE 2—Continued
Second Cooling of F-6—Continued

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
5.745	29.0	12.158	46.7	5.73772
5.726	21.6	12.146	49.0	5.72110
5.71	43.2	12.14	39.9	5.69960
5.69	51.2	12.144	30.2	5.67744
5.67	41.0	12.143	41.4	5.66005
5.65	25.8	12.126	54.5	5.64359
5.63	16.8	12.10	22.7	5.62574
5.62	29.2	12.08	52.5	5.61285
5.60	25.5	12.05	57.1	5.59356
5.58	19.7	12.02	67.0	5.57546
5.56	37.0	11.98	46.7	5.55116
5.54	47.0	11.94	39.0	5.52908
5.52	31.2	11.91	52.0	5.51252
5.50	15.2	11.88	27.0	5.49642
5.49	17.5	11.86	23.9	5.48577
5.48	20.0	11.84	22.4	5.47528
5.47	20.6	11.82	21.3	5.46509
5.46	19.7	11.80	21.6	5.45518
5.45	18.8	11.78	22.2	5.44542
5.44	18.0	11.76	24.3	5.43514
5.43	14.8	11.74	26.2	5.42638
5.42	31.5	11.71	50.3	5.41232
5.40	23.3	11.67	19.7	5.39458
5.39	16.4	11.65	30.4	5.38650
5.38	21.4	11.62	53.0	5.37428
5.36	29.2	11.57	52.8	5.35289
5.34	25.7	11.52	18.2	5.33416
5.33	28.0	11.49	53.5	5.32312
5.31	19.1	11.44	23.1	5.30546
5.30	19.4	11.41	21.3	5.29522
5.29	19.0	11.38	22.6	5.28542
5.28	16.6	11.35	24.9	5.27600
5.27	24.5	11.31	16.6	5.26404
5.26	18.3	11.28	23.0	5.25556
5.25	21.2	11.24	21.7	5.24506
5.24	17.8	11.20	21.6	5.23548
5.23	14.0	11.16	26.5	5.22646
5.22	23.0	11.10	59.3	5.21442
5.20	40.3	10.95	41.6	5.19018
5.18	18.2	10.85	25.3	5.17582
5.17	23.2	10.77	15.1	5.16394
5.16	17.7	10.72	21.8	5.15552
5.15	24.2	10.65	17.0	5.14413
5.14	17.2	10.60	22.7	5.13569
5.13	17.6	10.54	24.8	5.12585
5.12	17.3	10.48	23.2	5.11572
5.11	19.8	10.42	23.2	5.10573

TABLE 2—Continued
Second Cooling of F-6—Continued

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
5.10	21.0	10.36	19.7	5.09484
5.09	31.8	10.29	50.6	5.08226
5.07	15.6	10.20	24.0	5.06606
5.06	21.3	10.14	19.2	5.05613
5.05	25.8	10.08	15.1	5.04379
5.04	16.2	10.04	23.2	5.03589
5.03	22.8	9.98	17.8	5.02439
5.02	19.8	9.93	57.5	5.01488
5.00	18.0	9.83	22.1	4.99551
4.99	15.2	9.78	21.6	4.98587
4.98	18.0	9.73	22.0	4.97550
4.97	25.0	9.67	52.1	4.96351
4.95	26.2	9.57	51.2	4.94324
4.93	21.2	9.48	17.3	4.92449
4.92	23.2	9.43	16.1	4.91410
4.91	24.9	9.38	20.8	4.90455
4.90	20.8	9.33	45.8	4.89376
4.88	23.1	9.24	15.1	4.87394
4.87	26.4	9.19	11.7	4.86307
4.86	21.7	9.15	16.9	4.85438
4.85	16.5	9.11	21.3	4.84564
4.84	20.3	9.06	18.4	4.83476
4.83	23.5	9.01	13.5	4.82365
4.82	20.0	8.97	18.8	4.81485
4.81	24.0	8.92	51.7	4.80366
4.79	15.2	8.84	23.0	4.78601
4.78	21.7	8.79	16.0	4.77425
4.77	18.7	8.75	19.2	4.76503
4.76	24.5	8.70	14.3	4.75370
4.75	20.3	8.66	54.4	4.74456
4.73	24.0	8.57	13.7	4.72364
4.72	21.2	8.53	16.9	4.71443
4.71	28.3	8.48	47.5	4.70253
4.69	24.3	8.40	13.3	4.68354
4.68	13.5	8.37	24.3	4.67643
4.67	20.0	8.32	17.4	4.66465
4.66	18.8	8.28	18.2	4.65492
4.65	17.7	8.24	20.1	4.64532
4.64	16.6	8.20	21.2	4.63561
4.63	15.6	8.16	22.0	4.62585
4.62	15.3	8.12	22.9	4.61600
4.61	18.0	8.08	23.4	4.60565
4.60	13.8	8.04	24.0	4.59635
4.59	24.0	7.99	52.0	4.58369
4.57	22.8	7.91	14.0	4.56380
4.56	23.6	7.87	13.7	4.55367
4.55	25.3	7.83	13.2	4.54343

TABLE 2—Continued
Second Cooling of F-6—Continued

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
4.54	25.0	7.79	12.5	4.53334
4.53	25.8	7.75	13.0	4.52335
4.52	16.1	7.72	21.8	4.51575
4.51	16.4	7.68	20.0	4.50550
4.50	18.9	7.64	17.8	4.49485
4.49	21.0	7.60	17.0	4.48447
4.48	23.0	7.56	53.0	4.47394
4.46	27.0	7.48	12.2	4.45312
4.45	18.3	7.45	20.0	4.44524
4.44	20.6	7.41	17.3	4.43456
4.43	23.3	7.37	13.8	4.42372
4.42	16.6	7.34	22.2	4.41572
4.41	28.8	7.29	10.4	4.40266
4.40	20.5	7.26	15.4	4.39429
4.39	24.5	7.22	13.5	4.38355
4.38	18.0	7.19	20.6	4.37534
4.37	21.5	7.15	17.6	4.36450
4.36	14.2	7.12	24.4	4.35632
4.35	18.0	7.08	20.2	4.34529
4.34	22.2	7.04	16.0	4.33419
4.33	16.1	7.01	21.8	4.32576
4.32	20.6	6.97	17.8	4.31464
4.31	25.0	6.93	12.9	4.30430
4.30	19.0	6.90	19.0	4.29500
4.29	24.2	6.86	14.8	4.28379
4.28	18.0	6.83	19.9	4.27525
4.27	23.0	6.79	14.8	4.26379
4.26	17.8	6.76	19.3	4.25520
4.25	24.0	6.72	14.8	4.24382
4.24	18.0	6.69	19.1	4.23518
4.23	25.3	6.65	14.2	4.22360
4.22	19.1	6.62	19.2	4.21502
4.21	25.4	6.58	12.4	4.20328
4.20	21.0	6.55	17.3	4.19452
4.19	25.6	6.51	49.0	4.18314
4.17	29.6	6.44	46.5	4.16223
4.15	21.5	6.38	16.3	4.14431
4.14	17.5	6.35	20.3	4.13537
4.13	14.1	6.32	24.1	4.12631
4.12	21.6	6.28	16.0	4.11426
4.11	19.0	6.25	19.7	4.10509
4.10	26.7	6.21	48.0	4.09286
[†] 4.08				
4.03	30.3	5.98	44.3	4.02188
4.01	14.8	5.93	24.3	4.00622
4.00	11.8	5.90	26.5	3.99692

[†] Changed paper on chronograph.

TABLE 2—Continued
Second Cooling of F-6—Continued

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
3.99	34.0	5.85	42.1	3.98106
3.97	18.3	5.80	19.2	3.96512
3.96	29.3	5.76	16.5	3.94720
3.94	28.0	5.70	49.7	3.93279
3.92	24.8	5.64	11.6	3.91319
3.91	25.3	5.61	12.8	3.90338
3.90	12.8	5.59	25.2	3.89664
3.89	24.4	5.55	51.0	3.88354
3.87	37.2	5.48	39.5	3.86003
3.85	23.2	5.43	14.0	3.84376
3.84	13.2	5.41	25.2	3.83581
3.83	24.3	5.37	13.0	3.82348
3.82	13.2	5.35	25.3	3.81658
3.81	27.0	5.31	11.4	3.80619
3.80	16.0	5.29	22.8	3.79588
3.79	28.1	5.25	48.3	3.78264
3.77	17.3	5.20	20.3	3.76540
3.76	19.4	5.17	18.3	3.75485
3.75	21.2	5.14	16.7	3.74440
3.74	23.7	5.11	14.3	3.73376
3.73	25.1	5.08	51.5	3.72345
3.71	28.8	5.02	46.3	3.70234
3.69	34.9	4.96	42.0	3.68107
3.67	26.5	4.91	11.0	3.66293
3.66	30.8	4.88	47.0	3.65209
3.64	19.0	4.83	16.4	3.63463
3.63	25.7	4.80	10.4	3.62398
3.62	17.3	4.78	21.6	3.61555
3.61	20.7	4.75	17.5	3.60458
3.60	25.1	4.72	13.3	3.59346
3.59	29.3	4.69	48.8	3.58250
* 3.57				
3.52	21.5	4.51	28.2	3.51567
3.51	30.0	4.45	43.5	3.50184
3.49	29.8	4.40	47.8	3.47848
3.46	26.8	4.35	49.0	3.45292
3.44	27.3	4.30	51.2	3.43305
3.42	26.0	4.25	12.2	3.41319
3.41	19.0	4.23	20.8	3.40522
3.40	25.3	4.20	12.6	3.39332
3.39	17.9	4.18	20.0	3.38528
3.38	27.7	4.15	12.2	3.37306
3.37	19.0	4.13	19.5	3.36506
3.36	28.6	4.10	48.0	3.35260
3.34	30.3	4.05	17.8	3.32738
3.32	33.0	4.00	46.0	3.31165

* Chronograph stopped for several minutes.

TABLE 2—Continued
Second Cooling of F-6—Continued

Pt resistance	Time Pt to Fe	Fe resistance	Time Fe to Pt	Pt resistance corresponding to Fe resistance
ohms	secs.	ohms	secs.	ohms
3.30	18.8	3.96	20.1	3.29516
3.29	28.8	3.93	47.7	3.28248
3.27	18.2	3.89	14.0	3.26435
3.26	36.0	3.86	11.7	3.25245
3.25	18.2	3.84	20.8	3.24534
3.24	17.0	3.82	23.1	3.23576
3.23	26.8	3.79	12.2	3.22313
3.22	22.0	3.77	17.7	3.21446
3.21	16.2	3.75	23.1	3.20588
3.20	43.2	3.71	36.0	3.18909
3.18	17.9	3.68	19.9	3.17512
3.17	15.0	3.66	26.2	3.16633
3.16	25.8	3.63	11.6	3.15310
3.15	23.6	3.61	16.7	3.14415
3.14	18.9	3.59	21.2	3.13529
3.13	14.0	3.57	23.8	3.12630
3.12				

TABLE 3
Resistance in Ice and in Steam

	Pt	Fe (F-6)	Remarks
	Ohms	Ohms	
R ₀	1.4524	0.9713	R ₀ and R ₁₀₀ for both Pt and Fe same before and after second heating. For method of computing temperatures, see Scientific Paper 124.
R ₁₀₀	1.9987	1.5380	
F. I....	0.5463 $\delta=1.50$	0.6167	

ABSORPTION, REFLECTION, AND DISPERSION CONSTANTS OF QUARTZ

By W. W. Coblentz

An accurate knowledge of the transmission of quartz in the infra-red is essential in order to determine spectral energy curves of a black body with a quartz prism. As mentioned elsewhere, the program of investigation¹ of the radiation constants of a black body includes the employment of a quartz prism, which has a much larger dispersion than fluorite. Unfortunately, unlike fluorite, the absorption in quartz becomes quite marked at 2μ and is practically complete beyond 3μ . However, for the spectral region from the remote ultra-violet (0.25μ) to 1.7μ in the infra-red, quartz has the remarkable property of practically perfect transparency for the thicknesses (3 cm) which are ordinarily used in optical investigations. This is illustrated in the present research, where it is shown that after eliminating the losses for reflection at the interface, quartz air, the transmission is 100 per cent, if we admit an error of 2 parts in 1000. This property of great transparency in one spectral region, and great opacity in a closely adjoining region, requires the employment of thick samples of quartz in order to determine accurately the transmission in the intervening region. The whole investigation requires a special procedure, which one would not ordinarily undertake. The data obtained in the present investigation are therefore published with the hope that they may be of use to others.

A preliminary² examination of several samples of quartz was recently published. One sample consisted of two plates, each 6.5 mm in thickness. Inadvertently, as published, the thickness is stated to be 13 mm, with no mention that it represented two

¹ This Bulletin, 10, p. 2; 1913.

² This Bulletin, 9, p. 81; 1912.

plates. This explains the low transmission, caused by the four reflecting surfaces, as shown in the present paper, Fig. 1, curve *a*, where these data are reproduced. A second sample used in the preliminary examination consisted of a quartz prism, the ends of which were polished, through which the light passed, thus giving a layer 52 mm in thickness. The transmission (uncorrected for surface reflection) through this prism, given in Fig. 1, curve *b*, is of the order of 91.5 per cent, in the region of 1μ , which is the value found in the present work, using other material.

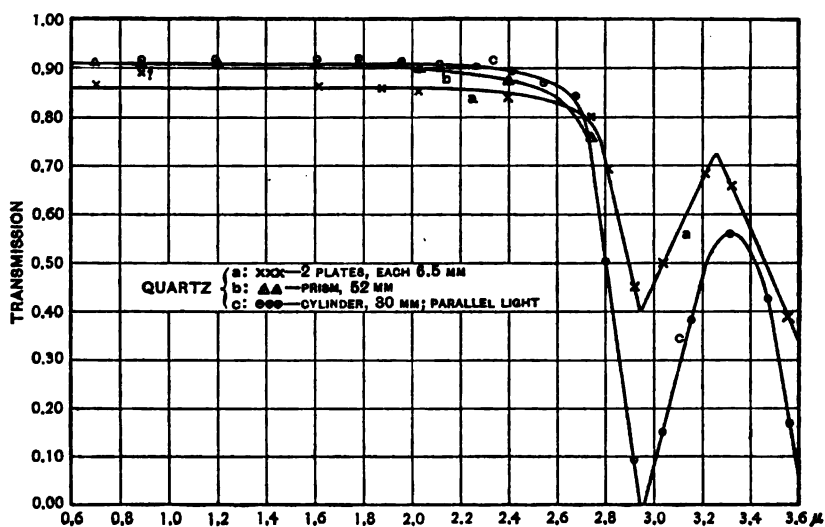


FIG. 1

In the preliminary test the source of radiation (a Nernst glower) was placed at a distance of about 10 cm from the spectrometer slit, through which the light passed, forming a narrow (8 to 10 mm wide) somewhat divergent beam upon the collimating mirror of the spectrometer. The quartz samples stood close in front of the spectrometer slit. The accuracy attained in the observations was not very high (1 per cent), owing to unsteadiness of the bolometer. In view of the fact that the light was not parallel^a

^a This, however, could do but little more than shorten the optical path. By actual measurement no variation in the width of the cone of light falling upon the collimating mirror could be detected when the thick quartz plate (the prism with polished ends) was placed before the slit. In the present research a mirror spectrometer fluorite prism and vacuum bolometer were used, as described in previous papers.

and that the transmission was not taken along the optic axis of the prism the investigation was undertaken anew, using two especially prepared cylinders of clear quartz. One cylinder was 50 mm in diameter and 29.925 mm in length. The faces were cut at an angle of about 40° to the optic axis and they had an unusually fine polish. The faces were plane to a fraction of a wave length of light, and they were parallel to within $1'$ of arc. This sample of quartz was perfectly free from smokiness, except at the extreme edge, which was shielded from radiation.

The second cylinder of quartz was 50 mm in diameter and 27.915 mm in thickness. The faces were cut perpendicular to the axis to within $49.5' \pm 0.5'$, the error in plane parallelism being about $0.5'$. This sample also showed faint traces of smokiness near the edge which was covered. The faces were not quite so highly polished as the first sample, which may account for the lower transmission (greater scattering) in the visible spectrum.

The source of energy was a seasoned Nernst glower operated on a storage battery. Fortunately, the observations happened to come on several calm, cloudy days, when the vacuum bolometer and galvanometer were perfectly steady, and the glower likewise was not affected by air currents. The rays from the glower were made parallel by means of a 50-cm focal length silvered mirror, and thence passed to a second mirror, 90 cm in focal length, which brought the rays to focus upon the spectrometer slit. A blackened diaphragm having an opening of about 3 by 3.5 cm was placed in the path of parallel rays. The quartz cylinder was mounted upon a suitable stage, sliding black and forth, close to and in the rear of the diaphragm (i. e., between the diaphragm and the second mirror). The ratio of the galvanometer deflection, observed when the quartz plate was over the opening in the diaphragm, to the deflection caused by the rays passing through the diaphragm without obstruction by the quartz, gave the transmission (Tr , Table 1). Atmospheric disturbances were unusually small, so that the galvanometer could be read to 0.1 mm, thus producing an accuracy of several parts in 1000 instead of a few parts in 100, which is the usual record of radiometric work.

The transmission curve, c , is given in Fig. 1, and the observations (Tr) are given in columns 3 and 6 of Table 1. In the transparent

region to 1.6μ the transmission is about 91.5 per cent, as previously observed on the prism which was almost twice as thick, with the (divergent) rays passing across the optic axis. Eliminating surface reflection from the observations on the two thin plates, previously investigated, curve *a*, Fig. 1, the data are in agreement with those of the thick plates.

In Table 1, columns 4 and 7, are given the true transmissions, T_o , of these two plates of quartz. These values are obtained by applying the well-known Fresnel formula for vitreous reflection, $R = \left(\frac{n-1}{n+1}\right)^2$ where n is the refractive index. The refractive indices (Table 3) of Carvallo and of Paschen were used.

TABLE 1
Transmission of Quartz

λ in mm	Reflection correction ($\frac{1-R}{1+R}$) ²	Quartz cylinder ($t=29.925$ mm)			Quartz cylinder ($t=27.915$ mm)		
		T_r (observed)	T_o	T_o^1	T_r (observed)	T_o	T_o^1
0.0005893	0.9125	0.9060	0.9929	0.9960	0.9055	0.9923	0.9958
.0006820	.9143	.9112	.9966	.9997	.9070	.9920	.9955
.0011971	.9153	.9145	.9991	1.0022			
.0016132	.9167	.9138	.9969	1.0000	.9135	.9966	1.0000
.0017835	.9173	.9143	.9967	.9998	.9140	.9964	.9999
.0019518	.9179	.9120	.9936	.9967	.9126	.9942	.9976
.0021128	.9185	.9092	.9898	.9929	.9106	.9914	.9948
.0022654	.9192	.9037	.9831	.9862	.9050	.9846	.9880
.0024098	.9199	.8967	.9748	.9778	.8979	.9761	.9795
.0025458	.9206	.8720	.9473	.9502	.8766	.9522	.9555
.0026120	.9209				.8626	.9367	.9399
.0026757	.9213	.8445	.9168	.9195	.8512	.9239	.9272
.0027392	.9216				.7757	.8417	.8446
.0028010	.9219	.5050	.5477	.5494	.5319	.5769	.5789
.0029213	.9227	.0917	.0994	.0997	.0748	.0811	.0814
.0030373	.9234	.153			.1426	.1544	.1549
.0031501		.384			.3776		
.0033132		.560			.5558		
.0034190					.5285		
.0034700		.430			.4573		
.0035690		.171			.1895		

The radiation contributed by two reflections $R^2(1-R)^2$ within the quartz plate is negligible in most work. If there were no errors of observation and no scattering of light, the values should be

$T_0 = 1$ in the spectral region where there is no absorption. From the present observations this appears to be true to about 2 parts in 1000 for the region of transparency from 0.6 to 1.8 μ . The fifth and eighth columns of Table 1 give the transmission T_0 on the assumption that there is perfect transmission up to and at $\lambda = 1.6132\mu$, i. e., all the observed values are divided by 0.9969, which is the observed value, T_0 , at $\lambda = 1.6132\mu$. The deviations from $T_0 = 1$ are then found to be far smaller than the average experimental errors which usually enter into such work.

TABLE 2
Transmission of Quartz—Extinction Coefficient

λ in mm	Quartz cylinder ($t = 29.925$ mm) κ	Quartz cylinder ($t = 27.915$ mm) κ	κ —Mean value
0.0016132	0.000 000 009	0.000 000 010	0.000 000 009
.0017835	.000 000 010	.000 000 012	.000 000 011
.0019518	.000 000 022	.000 000 021	.000 000 022
.0021128	.000 000 038	.000 000 035	.000 000 037
.0022654	.000 000 068	.000 000 066	.000 000 067
.0024098	.000 000 108	.000 000 109	.000 000 109
.0025458	.000 000 243	.000 000 235	.000 000 239
.0026120		.000 000 323	.000 000 323
.0026757	.000 000 410	.000 000 400	.000 000 405
.0027392		.000 000 894	.000 000 894
.0028010	.000 002 98	.000 002 92	.000 002 95

In passing it is desirable to record the very marked reflection caused by fine particles of dust. One sample of quartz, which had stood uncovered for a day, transmitted over 1 per cent (depending upon the wave length) less than the usual value (89.8 instead of 91.35 per cent). Examined in front of a bright incandescent lamp, the surfaces showed faint tarnishing and dust. After thoroughly polishing the surfaces with a soft cloth the normal transmission (91.4 per cent) was again observed.

The absorption index (extinction coefficient) κ is computed from the equation $A = 1 - e^{-a}$, where $a = 4\pi \frac{n\kappa}{\lambda}$. Here the thickness, l , of the plate and the wave length, λ , are in millimeters. The data for the two samples, computed from columns 4 and 7 of

Table 1, are given in Table 2, the values being in close agreement where the true absorption of quartz becomes important. A large absorption band of quartz occurs at 2.95μ ; and a small depression at 2.6μ (see Fig. 2) was observed in the transmission of both samples of quartz. The sample of quartz, 27.915 mm in thickness, was not so highly polished as the first specimen. This would cause more scattering of light, and an apparently high extinction coefficient, especially in the visible spectrum.

TABLE 3

Quartz Reflection

[In this table R is the reflection which occurs at normal incidence and R_1 and R_2 are the reflection coefficients for light polarized respectively in and perpendicular to the plane of incidence.]

λ	$(1-R)^2(1+R^2)$	$\frac{(1-R_1)^2+(1-R_2)^2}{2}$	Refractive index	λ	$(1-R)^2(1+R^2)$	$\frac{(1-R_1)^2+(1-R_2)^2}{2}$	Refractive index
0.325 μ	0.9062	0.8668	1.57094	1.0417		0.8821	1.53442
.340	.9069		1.56744	1.0715	0.9149		1.53402
.3582	.9077		1.56400	1.1592		.8827	1.53283
.361	.9078		1.56348	1.2215	.9154		1.53201
.396	.9091	.8722	1.55815	1.3070		.8835	1.53090
.4046	.9094		1.55706	1.376	.9159		1.53001
.410	.9095		1.55649	1.4219		.8842	1.52942
.434	.9101	.8740	1.55396	1.528	.9164		1.52800
.4862	.9113		1.54964	1.5414		.8848	1.52781
.508	.9115	.8764	1.54822	1.670	.9169		1.52602
.5349	.9119		1.54663	1.6815		.8856	1.52583
.5893	.9125	.8780	1.54420	1.7614		.8860	1.52468
.6158	.9127	.8785	1.54323	1.870	.9176		1.52302
.643	.9129	.8789	1.54226	1.9457		.8872	1.52184
.6563	.9130		1.54182	1.999	.9181		1.52100
.6678	.9131		1.54155	2.170	.9188		1.51802
.686	.9133	.8794	1.54097	2.1719		.8886	1.51799
.7065	.9134		1.54048	2.3573		.8900	1.51449
.7435	.9136		1.53956	2.384	.9198		1.51403
.760	.9137	.8802	1.53917	2.574	.9207		1.51002
.7682	.9138		1.53890	2.6519		.8925	1.50824
.7711	.9138		1.53895	2.746	.9216		1.50602
.8007	.9139	.8805	1.53835	2.7993		.8938	1.50474
.8325	.9141		1.53773	2.904	.9226		1.50201
.8671	.9142	.8810	1.53711	3.058	.9235		1.49800
.9047		.8813	1.53649	3.0939		.8967	1.49703
.9335	.9145		1.53600				

The factors for eliminating the absorption in a wedge of quartz are determined from the equation ⁴

$$\frac{I_0}{I} = \frac{\log (1 - A)^{B/l}}{[(1 - A)^{B/l} - 1] \log \epsilon}$$

It is derived from an integration of the equation

$$I = \frac{I_0}{h} \int_0^h \epsilon^{-\frac{B}{h}x} dx.$$

In these equations A is the absorption $(1 - T_0)$ observed in the quartz plate and l is its thickness (29.925 mm); B is the thickness of the back of the prism (i. e., the width of the face, 52 mm, which is opposite the refracting angle); and h is the vertical height of the refracting edge from the back of the prism. The observed intensity (in galvanometer deflections), is I ; and I_0 is the true intensity of the radiations emanating from the source.

TABLE 4

Factors for Eliminating the Effect of Absorption in a Prism Having a Base (Back Face) of 50 to 52 mm in Width

λ in mm	Factor			
	$t=29.925$ mm	$t=27.915$ mm	Mean	$\frac{\text{Mean}}{1.000}$
0.0016132	1.0028	1.0032	1.0030	1.0000
.0017835	1.0029	1.0034	1.0032	1.0002
.0019518	1.0057	1.0055	1.0056	1.0026
.0021128	1.0089	1.0082	1.0086	1.0056
.0022654	1.0150	1.0147	1.0149	1.0119
.0024098	1.0226	1.0229	1.0228	1.0197
.0025458	1.0483	1.0467	1.0475	1.0444
.0026120		1.0628	1.0628	1.0596
.0026757	1.078	1.076	1.077	1.074
.0027392		1.117	1.117	1.114
.0028010	1.619	1.605	1.612	1.607

In Fig. 2 curve A , gives the true transmission (T_0 of Table 1) of the thickest plate of quartz. The absorption begins at 1.8μ . Curve B , Fig. 2, gives the factors to be used in eliminating the effect of this absorption in a prism, the back face of which is 50 to 52 mm in thickness. Numerical data for eliminating this absorption, which begins at about 1.9μ , are given in Table 4. This table shows

⁴ Paschen, Sitzber. Akad. Wiss., Berlin, 22, p. 405, 1899.

that, for example, at 2.739μ the observed intensity must be increased by 11.4 per cent in order to correct for the loss by absorption in the prism. The last column in Table 4 gives the correction for absorption in the prism on the assumption that the error of the present observation is 0.3 per cent. It is obtained by dividing all the mean values by 1.003.

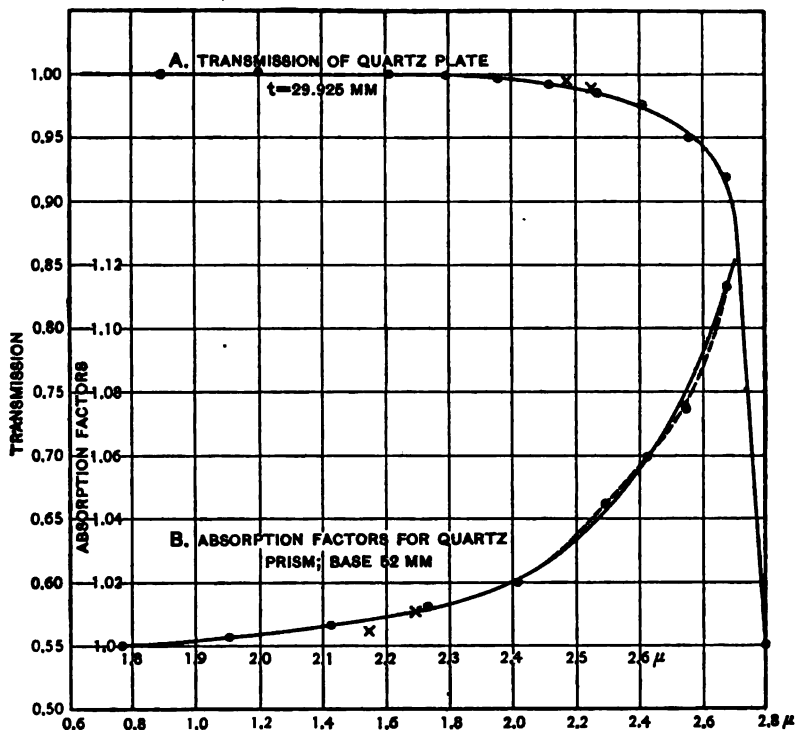


FIG. 2

A further increase in the value of I is, of course, necessary for the loss by reflection from the prism faces with variation in the angle of incidence which is required in order to cause the rays to pass through the prism at minimum deviation. The values for reflection were computed by means of the Fresnel formulas,

$$R_1 = \frac{\sin^2(i-r)}{\sin^2(i+r)} \quad R_2 = \frac{\tan^2(i-r)}{\tan^2(i+r)},$$

which give the variation in reflection with variation in the angle of incidence. The angles of incidence used in this computation are those required in order that the rays will pass at minimum deviation through a quartz prism having an angle of $59^{\circ} 51' 21''$. These values may be used without serious errors with a prism having a refracting angle which differs by $5'$ to $6'$ from the one used in the present computations. The numerical data for eliminating the variation in reflection with variation in angle of incidence are given in column 3 of Table 3. For a prism having a refracting angle of 60° the values should be decreased by 0.0005.

If the spectral energy measurements are made with a radiometer which is covered with a quartz window then a still further correction for reflection (also for absorption) must be made to the observations. This correction for reflection is the same as the one applied in determining the transmission of quartz. The numerical values for correcting for the reflection from a quartz window are given in column 2 of Table 3. In Fig. 2, curve B, the crosses ($\times \times$) show the absorption in a plate of quartz 3.5 cm in thickness. They represent preliminary data, observed by Warburg⁶ and his associates.

To obtain an accurate calibration curve of a prism is a laborious process and these data are included in Table 5 of the present paper. The calibration curve (minimum deviation settings of the spectrometer circle and wave lengths) was computed from the refractive indices of Carvallo⁶ and of Paschen.⁷ The fiducial line is the yellow helium line; $\lambda = 0.58758\mu$.

The data pertain to a quartz prism having a refracting angle of $59^{\circ} 51' 21''$. Hence, for a prism having a considerably different angle the wave lengths will be found to be in error. However, the "slit-width factors" for reducing an energy curve from prismatic to normal spectrum will not be affected by the usual deviations from a 60° prism. These factors relate to a radiometer receiver $10'$ in width, and they may be used for slit widths at least 50 per cent different from this value. For example, the test was made for a width of $6'$, which should give slit-width

⁶ Warburg, Leithäuser, Hupka, Müller, *Ann. der Phys.* (4), 40, p. 614; 1913.

⁶ Carvallo, *Compt. Rendus*, 126, p. 728; 1898.

⁷ Paschen, *Ann. der Phys.*, (4), 38, p. 1005; 1911.

factors which are 0.6 of those given in Table 5. By reading the wave lengths from the calibration curve for a difference of 6' on the spectrometer circle, the wave lengths subtended by a radiometer, 6' in width, in different parts of the spectrum were found in agreement to within 2 parts in 10 000 with the values (i. e., 0.6 of the values) in Table 5, which is as accurate as one can read the values from the calibration curve.

TABLE 5
Quartz Prism Calibration

Spect. setting	Wave length	Slit width—10'	Spect. setting	Wave length	Slit width—10'	Spect. setting	Wave length	Slit width—10'
° /	μ	μ	° /	μ	μ	° /	μ	μ
+2 30	0.3206		15	0.5269	0.0340	-2 00	1.9496	0.1178
25	.3242	0.0075	10	.5451	.0385	05	2.0073	.1148
20	.3281	.0080	05	.5654	.0425	10	2.0644	.1118
15	.3322	.0082	0 00	.58758	.0465	15	2.1191	.1089
10	.3363	.0084	- 05	.6119	.0507	20	2.1733	.1061
05	.3406	.0089	10	.6383	.0562	25	2.2252	.1032
+2 00	.3452	.0093	15	.6681	.0637	30	2.2765	.1004
55	.3500	.0096	20	.7020	.0717	35	2.3256	.0978
50	.3550	.0100	25	.7398	.0808	40	2.3743	.0954
45	.3600	.0105	30	.7828	.0902	45	2.4210	.0932
40	.3652	.0109	35	.8300	.1004	50	2.4675	.0914
35	.3708	.0118	40	.8832	.1100	55	2.5124	.0896
30	.3764	.0122	45	.9400	.1198	-3 00	2.5571	.0878
25	.3827	.0128	50	1.0025	.1285	05	2.6002	.0862
20	.3889	.0135	55	1.0685	.1365	10	2.6433	.0845
15	.3959	.0144	-1 00	1.1390	.1418	15	2.6847	.0829
10	.4029	.0151	05	1.2103	.1445	20	2.7262	.0814
05	.4108	.0162	10	1.2835	.1454	25	2.7661	.0798
+1 00	.4193	.0176	15	1.3557	.1444	30	2.8060	.0784
55	.4284	.0185	20	1.4279	.1425	35	2.8445	.0771
50	.4378	.0195	25	1.4982	.1397	40	2.8831	.0758
45	.4479	.0213	30	1.5676	.1369	45	2.9203	.0746
40	.4591	.0226	35	1.6351	.1337	50	2.9577	.0735
35	.4705	.0239	40	1.7013	.1304	55	2.9938	.0723
30	.4830	.0260	45	1.7655	.1274	-4 00	3.0300	.0712
25	.4965	.0281	50	1.8287	.1240	05	3.0650	.0703
20	.5111	.0304	55	1.8995	.1209	10	3.1003	

The manner of obtaining the calibration curve and slit-width correction factors is given more fully elsewhere.^a In Table 5 the "spectrometer setting" is the minimum deviation setting. If

^a This Bulletin, 10, p. 2; 1913.

a Wadsworth mirror-prism device is used, the angular rotation is only half as great to attain the wave length here recorded.

In conclusion, acknowledgement is due to my assistant, W. B. Emerson, for the numerous computations involved in this investigation.

SUMMARY

This paper gives quantitative data on the absorption, reflection, and dispersion of quartz, extending from the ultra-violet to 3μ in the infra-red. The data may be used in determining spectral energy curves. Quartz is practically transparent from the ultra-violet to 1.8μ . It begins to absorb strongly beyond 1.8μ , and tabulated data are given for eliminating the effect of this absorption in a quartz prism. The results show that (within the errors of observation) in unpolarized light, the transmission is not affected by the direction in which the radiations pass through the material with respect to the optic axis.

WASHINGTON, December 9, 1913.

CHARACTERISTIC EQUATIONS OF TUNGSTEN FILAMENT LAMPS AND THEIR APPLICATION IN HETEROCHROMATIC PHOTOMETRY¹

By G. W. Middlekauff and J. F. Skogland

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¹ A preliminary paper on this subject was read at the Eighth Annual Convention of the Illuminating Engineering Society, Cleveland, Ohio, Sept. 21-24, 1914.

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I. INTRODUCTION

This investigation was carried out at the Bureau of Standards with a view to finding a more satisfactory method than those at present in vogue for overcoming the difficulties due to color difference when lamps of higher or lower efficiency are to be compared with the carbon primary standards. In order that the application of characteristic equations in this connection may be fully understood, it is deemed advisable, before discussing the main problem at issue, to first give a brief description of the character of the standard photometric work of the Bureau, the methods employed, and the principal difficulties encountered.

II. STANDARD PHOTOMETRIC WORK AT THE BUREAU OF STANDARDS

1. THE PRIMARY PHOTOMETRIC STANDARDS

The photometric standards, by means of which the international candle is maintained at the Bureau of Standards, are a group of carbon filament incandescent lamps operated at an efficiency of

4 watts per mean horizontal candle. On account of photometric difficulties which are involved in comparing lights of different color, and which increase as the color difference increases, it is fortunate that these primary standards occupy a position at about the middle of the range of color of lamps now used as secondary and working standards, being blue in comparison with the Hefner and other flame standards and red in comparison with tungsten lamps when operated at or near normal efficiency. Even with the primary standards in this intermediate position, the color difference met with in many cases is considerable and very troublesome in standard photometry where the highest accuracy is required.

2. CLASSES OF LAMPS SUBMITTED FOR STANDARDIZATION

In general there are two classes of lamps submitted to the Bureau of Standards for certification, (a) flame lamps, of which practically all are pentane and (b) electric incandescent lamps, of which during the past year one-third were carbon and two-thirds tungsten.

(a) FLAME LAMPS

Although different forms of flame lamps have been recognized as primary standards (for example, the Carcel in France, the Hefner in Germany, and the pentane in England) none of them is now considered entirely satisfactory for this purpose.³ Though made and used according to official specifications, individual lamps differ among themselves by amounts considerably greater than the errors of photometric measurement. Incandescent lamps, on the other hand, when operated at a definite voltage at which they have been standardized in terms of a light unit agreed upon, will maintain that unit constant with an accuracy far above that which is possible with flame standards. With so much in favor of incandescent lamps, it is perfectly reasonable that they, in preference to any of the present so-called primary-flame standards, should be chosen to maintain the international candle constant, at least until a lamp appears the value of which can be satisfactorily reproduced from specifications. Accordingly in this country, the real primary standard is a group of incandescent lamps, and the various flame standards which are assigned values by comparison

³ Ross and Crittenden, "Flame Standards in Photometry." *This Bulletin*, 10, p. 557; 1924. (Scientific Paper No. 222.)

with the primary carbon standards have become secondary standards, and their specifications are practically ignored except by the makers.

In the photometry of pentane lamps the measurements are made directly in terms of carbon working standards operating at a low efficiency (about 7 watts per candle) so as to match the pentane flame in color. As this color is practically the same for all pentane lamps and remains constant under normal working conditions, only one group of electric working standards is required, and the color difference involved in checking them in terms of the primary standards is the same from time to time. In so far as the preparation and maintenance of working standards are concerned, the standardization of pentane lamps is therefore simple in comparison with that of electric incandescent lamps.

(b) **ELECTRIC INCANDESCENT LAMPS**

On account of the great flexibility, as to color, of the incandescent lamp, especially of the tungsten lamp, when supplied with current at different voltages, the range of color through which it may be used as a standard extends from the dull red of initial incandescence to comparative blue at normal efficiency. Even normal efficiency is not a fixed value but has been and is still steadily increasing with improvements in manufacture. The Bureau, therefore, as custodian of the primary standards, must be in a position to calibrate incandescent lamps at a large number of efficiencies, and hence a single group, or even a number of groups, of working standards, each group of some definite color, can not meet the desired condition of color match with any given lamp that may be submitted for test.

It is obvious, therefore, that, with the exception of carbon lamps at 4 watts per candle, the standardization of practically every lamp submitted involves, either directly or indirectly, a color difference in the photometric measurements.

3. DIFFICULTIES DUE TO COLOR DIFFERENCE

Comparison of lamps of the same color involves no special difficulties and comparatively little experience is required to enable an observer to produce results of considerable accuracy. But when a color difference exists, even observers of experience do not

agree in their photometric measurements, the disagreement being due principally to two causes, (1) difference in color vision and (2) difference in judgment as to what constitutes a match in intensity, thus rendering it difficult for an individual to repeat even his own observations with the precision possible when there is a color match. Hence, to establish standards, it is not only necessary to have observers of normal color vision but also to obtain a very large number of readings by experienced observers who have learned to fix and maintain a suitable criterion so that they can obtain consistent results at different times.

III. METHODS OF HETEROCHROMATIC PHOTOMETRY

In the photometry of differently colored lights at least four methods have been used, viz, visual acuity, critical frequency, equality of brightness, and flicker. Of these, only the last two mentioned are sufficiently sensitive for the accuracy required in precision work.* In the experience of the Bureau of Standards more consistent results have been obtained by the equality of brightness than by the flicker method, and for this reason the Lummer-Brodhun contrast photometer, which makes use of the equality of brightness principle, has been used for all photometric work, both for lights of the same color and of different color.

IV. ELIMINATION OF COLOR DIFFERENCE IN ROUTINE WORK

In the Bureau's regular routine work of standardizing lamps of high efficiency (i. e., blue in comparison with carbon standards) the measurements, so far as is possible, are made with color match obtained either by the use of blue-glass screens placed in the path of the light from the carbon working standards or by the use of tungsten working standards of approximately the color of the lamps to be measured. The latter may be a group of standards each operated at a single voltage (or color) or a group whose candle-power values are known through a considerable range of color. However, it is the common practice, especially when important standards are submitted, to make measurements in terms of all three groups.

* Ives, H. E.; *Phil. Mag.*, 24, p. 156; 1912.

1. USE OF COLOR SCREENS

Obviously either red or blue screens of the proper spectral absorption may be used to eliminate color difference. Up to the present, however, red screens of sufficient transparency, for most purposes, have not been obtainable, hence all color matching of test lamps with the primary standards has been done with blue glasses, which can be obtained with almost any desired degree of color absorption and very uniform throughout.

2. USE OF SECONDARY STANDARDS

Evidently the best way of eliminating color difference in the photometry of any light source is by the use of a standard of the same kind. Hence it is an advantage to use electric incandescent standards when measuring lamps of this kind. Fortunately, the tungsten lamp is so flexible as to color adjustment that it can be made to match all incandescent lamps, regardless of the material of the filament. Further than this, it can be made to match, at least very approximately, the color of every flame lamp used as a standard. It is, therefore, an ideal working standard in heterochromatic photometry. It has an advantage over the use of color screens in that it will match the test lamps at whatever efficiency they may fall, but it has the disadvantage of being less durable.

Although both methods are satisfactory in the elimination of color difference in routine work, both transfer rather than dispose of the difficulties which must be met in the calibration of the screens and the standardization of the lamps. As secondary tungsten standards have usually been standardized at the Bureau by the use of glass screens, the problem of stepping from one color to another has been reduced to the calibration of the screens.

V. CALIBRATION OF COLOR SCREENS

The calibration of color screens as done heretofore introduces deviations in observed values fully as great as those which obtain in the direct comparison of lamps of different color. This renders the derivation of reliable values a more difficult matter than would at first appear. Even after a reliable value is obtained, the advantage of measurements at a color match is not fully realized,

because the range in efficiency through which a given screen eliminates color difference is rather narrow. For the best results a different screen should be used for each efficiency, and the calibration of each screen means that the same difficulties must again be encountered. It was primarily with a view of finding a method of reducing both the errors and the amount of labor involved in these calibrations that this investigation was undertaken.

1. OLD METHOD, INVOLVING COLOR DIFFERENCE

The most direct method of determining the percentage transmission (or transmission coefficient) of a color screen for use with a source of 4-wpc-carbon color is as follows: The photometer is arranged as for the ordinary comparison of two lamps A and B, of which A is adjusted to 4-wpc-carbon color. The screen is placed at the side of the photometer head in the path of the light from this lamp, and B is adjusted to match the transmitted light in color. A photometric setting is then made with the screen in position and another with it removed. The ratio of the first setting to the second gives the coefficient of the screen independently of the values of A and B. The test may be varied by adjusting B to color match A when the screen is removed, or B may be adjusted to a color anywhere between those of the direct and transmitted light from A. In every case, however, at least one of the two settings required must be made with a color difference, thus involving all the difficulties and uncertainties of the photometry of differently colored lights.

In the calibration of the screen it is important that lamp A be of the same color as the light source with which the screen is to be used, otherwise the coefficient will have a different value depending upon the color of the incident light.

2. PROPOSED METHOD, USING VOLTAGE CANDLEPOWER RELATION

In order to avoid measurements involving color difference when making such calibrations the following method is proposed: Both sources A and B are tungsten lamps. A is first adjusted in voltage (to about 3.1 wpc) to match 4-wpc-carbon color, and B is adjusted as before—that is, to a color match with the

light transmitted by the screen. After making a photometric setting, the screen is removed and, with B constant, A is increased in voltage until it matches B in color, and a second setting is made. Calling the settings S_1 and S_2 and the two candle power values of A, C_1 and C_2 , respectively, the coefficient of transmission is $T = \frac{S_1}{S_2} \cdot \frac{C_2}{C_1}$. As both settings are made with a color match, all the difficulties involved in the method first given above are eliminated, close agreement among different observers results, and T is determined with comparatively little labor.

This method, however, assumes that the ratio $\frac{C_2}{C_1}$ has been accurately determined, which can be easily done in terms of the corresponding observed voltages, provided the voltage-candle-power relation for lamp A is known with sufficient accuracy. The method, therefore, transfers the special difficulties of the direct comparison of lights of different color, not to the calibration of the proper screens for color match but to the problem of determining accurately the variation of candlepower with voltage. As this variation must follow some regular law, there was hope of finding an equation which would represent it over a considerable range. As the results of this paper will show, this hope was more than realized, as there was found a simple equation so general in form as to express the variation with voltage, not only of candlepower but also of wattage, current, and wpc, with a high degree of precision over a much wider range than was at first anticipated.

By the use of this equation values observed at different voltages (or wpc) can be so adjusted as to bring them into harmony with one another, and, hence, there is obtained at all points of observation an accuracy greater than would be possible if independent measurements were made at the various points on unrelated quantities like the transmission of different color screens.

The method also makes it possible to obtain accurate values at any point in terms of values at any other point within the range through which the equation is known to hold. Hence, within this range, a tungsten lamp, the value of which at any given voltage (or wpc) is known, may be used as a standard at

color match with any light source to be measured, the value of the standard at that color being accurately determined by computation from the corresponding observed voltage. All measurements are thus made at color match without the use of color screens, which may be entirely discarded except only as auxiliaries in making check measurements.

In case screens are to be used, their calibration is accomplished as outlined above, the value of the ratio $\frac{C_2}{C_1}$ being accurately determined by means of the equation.

VI. MEASUREMENT OF LAMPS FOR CHARACTERISTIC RELATIONS

1. THE LAMPS INVESTIGATED

The group first investigated was composed of seven 60-watt, 110-volt tungsten standards whose constancy had been well established. The filaments of these lamps were "formed" drawn wire comprising four hairpin loops, with legs welded in series to the bottom radial anchors. The forming process having removed the elasticity at the bend, the loop retains its form without varying the pressure on the top supports. The latter were light molybdenum wires, each with a helical coil between the loop supporting the filament and the end fused into the central hub. This arrangement gives an elastic mount resulting in ready adaptation to expansion and contraction of filament without sag, and a steady value of current is reached very soon after the lamp is placed in circuit.

Other groups of lamps investigated are described later.

2. THE STANDARDS EMPLOYED

As the above lamps were to be run at 12 voltages corresponding to efficiencies ranging from about 3.8 to 1.1 wpc, it was decided to divide the measurements so as to secure values in terms of carbon and tungsten working standards, with an approximately equal range of color against each group of standards.

Consequently, from the lowest voltage to that corresponding to about 2.0 wpc, carbon working standards were used. Measurements at higher voltages were made against tungsten working

standards. It is evident, therefore, that there was a considerable range in color between standards and test lamps running from reddish (relatively low efficiency) to bluish (relatively high efficiency) against each group of standards. But as the average results of the five observers who made the measurements on these lamps had been found to be the same as that of a much larger group of equally experienced observers when a color difference was involved in the photometric measurements, it is believed that the results obtained in these measurements are such as would be obtained by an average or normal eye.

(a) CARBON STANDARDS

These standards operate at the same color as the primary standards with which they are kept in check by frequent inter-comparisons. When matching the carbon standards in color the tungsten lamps operate at about 3.1 wpc.

(b) TUNGSTEN STANDARDS

The normal operating efficiency of these standards is approximately 1.5 wpc. Their candlepower and current values have been indirectly verified by the National Physical Laboratory of England, as agreement in candlepower and current values on several groups of lamps (which the tungsten working standards reproduce) was obtained between the National Physical Laboratory and the Bureau as the result of careful measurements by each laboratory, several different methods having been employed.

3. APPARATUS

All measurements of candlepower were made on a double photometer,⁴ thus affording a valuable check of one observer against the other. The individual settings were recorded on a chart⁵ by a special printing device auxiliary to the photometer. By this method of recording the observer is entirely unprejudiced in his settings. Voltage and current were measured simultaneously by means of two potentiometers. The chart referred to contains a printed candlepower scale from which the values of lamps under

⁴ Described by Rosa and Middlekauff, *Proc. A. I. E. E.*, **29**, p. 1191; 1910.

⁵ Described by G. W. Middlekauff, this *Bulletin*, **7**, p. 11; 1911. Scientific Paper No. 144.

test may be read off directly in terms of the standards. Thus are avoided the labor and possible errors involved in computing the candlepower values from readings made from a centimeter or other divided scale on the photometer bar.

4. OBSERVED VALUES

In order to avoid a repetition of tables, the observed and computed values for these lamps are given together in Tables 5 and 6, to which reference should be made at this point. (See pp. 503-504.) The two lamps (Nos. 2658 and 2660) exhibited in Table 5 were selected as best representing the group of seven. The observed values given for each lamp are the means of all values obtained by the various observers, there being an average of about seven at each voltage. Each observed value is the average of from 10 to 40 individual photometric settings represented by a corresponding number of points on the record chart.

5. ACCURACY OF THE MEASUREMENTS

Of a total of about 680 individual observed values, about 5 per cent, having comparatively large deviations from the mean, were discarded for reasons considered justifiable. After this procedure, the mean of the remaining observations at each voltage for each lamp was accepted as the observed value and is so designated in what follows.

At the individual voltages the deviation from the accepted mean observed value ranged from 0.7 to 0.2 per cent, the mean deviation being 0.45 per cent. Deviations at color match with carbon and with tungsten standards were approximately equal and were very close to the mean value of 0.45 per cent.

VII. CHARACTERISTIC EQUATIONS

1. FORM OF EQUATIONS PREVIOUSLY USED

Characteristic equations most commonly used heretofore have been of the constant exponent form,⁶ $y = ax^b$, the range of application having been usually admitted to be comparatively limited;

⁶ A. S. Merrill, *Trans. A. I. E. E.*, **29**, p. 959; 1910.

or of the form $y = ax^b [1 + cx + dx^2]$ in which x is a variable ratio (e. g., voltage ratio) and a , b , c , and d are constants. The second equation, though considerably more general than the first, does not fit the observed values herein given with the accuracy required for the present purpose. In actual practice, however, the method most generally followed has been to draw curves through observed values without reference to their equations. A modification of this method ⁷ involves the use of the slope of the characteristics as exponents.

2. FORM OF EQUATION ADOPTED BY THE AUTHORS

As a logarithmic graph of the observed values of voltage and candlepower obtained in this investigation indicated a smooth curve for each lamp, an empirical equation of the form $y = Ax^2 + Bx + C$ was assumed, in which $y = \log$ candlepower and $x = \log$ volts, A , B , and C being constants. This is equivalent to the assumption that the rate of change of the slope is constant and equal to $2A$, i. e., $\frac{d^2y}{dx^2} = 2A$. This is the first proposal of an equation of this form, although it is the form logically required to produce a smooth curve on logarithmic paper.

The slope, $\frac{dy}{dx} = 2Ax + B$, corresponds to the differential coefficient mentioned by Cady ⁸ and its evaluation gives a factor which may be used for correction from observed values to other values within a small range. A discussion of this equation and its application to certain problems will be given later (p. 514).

The equation expressing the relation of volts to watts was found to be of the same form, y indicating $\log$ watts in this case.

Since $\log \text{ wpc} = \log \text{ watts} - \log \text{ cp}$, the constants in the equation expressing the relation of volts to wpc, are obtained by subtracting those of the voltage-candlepower equation from those of the voltage-wattage equation. Similarly, since $\log \text{ amperes} = \log \text{ watts} - \log \text{ volts}$, the equation expressing the relation of volts to amperes is of the form $y = Ax^2 + (B - 1)x + C$, the constants A , B ,

⁷ F. E. Cady, *Elec. Rev. & West. Elec.*, 59, p. 1092; 1911.

⁸ E. J. Edwards, *Gen. Elec. Review*, 17, p. 283; 1914.

⁹ *Elec. Rev. & West Elec.*, 59, p. 1091; 1911.

C having the same values, respectively, as in the voltage-wattage equation. It is, therefore, necessary to solve only two equations expressing the relations, voltage to candlepower, and voltage to wattage (or voltage to current).

The equations expressing these two relations were then solved for each lamp of the group by the method of least squares, Gauss's method of substitution and successive reduction being employed, the results giving A , B , and C , respectively, for each equation, and from these equations all the others were derived.

As the slope of the curve represented by these equations is a function of the wpc, it is evident that either to compare similar curves of the various lamps or to determine a mean value of each variable for the group, it is necessary to choose some value of wpc as a basis and to express the values of the dependent variables in terms of (or percentages of) the values corresponding to the chosen basis. For the sake of brevity, the wpc basis and the corresponding values of all the variables will be hereafter referred to as normal values.

It is entirely immaterial what efficiency is chosen as normal, but for this group of curves 1.20 wpc was found most convenient, and for this reason it was selected. As will be shown later, it is a simple matter to change to any other normal wpc, if it is so desired.

By assuming the values of all variables, except wpc, to be unity at normal efficiency (1.20 wpc) the constant C disappears from every equation except the one for wpc evaluation, where it has the value 0.07918 (i. e., $\log 1.20$).

As all the equations expressing the relation of x to the other variables are of the same form, they may be written together in the general equation

$$y_n = A_n x^2 + B_n x + C$$

where $C = 0$ except when $n = 1$, the quantities signified by $n = 1, 2, 3$, and 4 , respectively, being as given in the following section.

3. THE FUNDAMENTAL EQUATIONS

The fundamental equations and the most important equations derived from them are given in Table 1. In these equations,

$$\begin{aligned}x &= \log \text{ voltage ratio,} \\ y_1 &= \log \text{ actual wpc,} \\ y_2 &= \log \text{ candlepower ratio,} \\ y_3 &= \log \text{ wattage ratio,} \\ y_4 &= \log \text{ current ratio,}\end{aligned}$$

and the conditional relation among these quantities is that

$$x = y_2 = y_3 = y_4 = \log 1 = 0, \text{ when } y_1 = \log 1.20 = 0.07918.$$

TABLE 1

Characteristic Equations

$$y_1 = 0.918x^2 - 2.009x + 0.07918 \quad (1)$$

$$y_2 = -0.946x^2 + 3.592x \quad (2)$$

$$y_3 = -0.028x^2 + 1.583x \quad (3)$$

$$y_4 = -0.028x^2 + 0.583x \quad (4)$$

Equations derived from the above:

$$x = 1.09490 - 1.0439\sqrt{1.02073 + y_1} \quad (1a)$$

$$x = 1.89870 - 1.0282\sqrt{3.41000 - y_2} \quad (2a)$$

$$y_1 = 2.88028 - 1.5169\sqrt{3.41000 - y_2} - 0.970y_2 \quad (5)$$

$$y_2 = 1.74682 - 1.5878\sqrt{1.02073 + y_1} - 1.031y_1 \quad (5a)$$

These derived equations are obtained as follows: 1a and 2a from 1 and 2, respectively, by expressing x in terms of the corresponding y ; 5 from 1 and 2 by the elimination of x ; and 5a from 5 by expressing y_2 in terms of y_1 . In many problems the equations expressed in this form will be found more convenient than in the original form.

Since equations 1 to 4 are quadratics, there are two values of x which satisfy each. For example, in equation 1a, $x = 1.09490 \pm 1.0439\sqrt{1.02073 + y_1}$. The conditional relation that $x = y = 0$ when $y_1 = 0.07918$ leads to the selection of the value in which the last term is negative. Similar reasoning applies to the other three equations also.

4. METHOD OF REDUCING TO ANY WPC BASIS

(a) REDUCTION OF THE FUNDAMENTAL EQUATIONS

In passing from 1.20 wpc to any other wpc as a basis, no change occurs in the form of the general equation

$$y_n = A_n x^2 + B_n x + C. \quad (6)$$

Even the constant A_n remains unchanged, because, by the fundamental assumption made in choosing this form of equation, the rate of change of slope, $\frac{d^2 y}{dx^2}$, is constant and equal to $2A_n$, irrespective of the value of the wpc chosen as normal. The conditional relation among the variables determines the value of the constant C , that is, the log of the normal wpc. Hence, in passing to the new basis, a new value C' (=log new basis) is at once assigned to this constant. The constant B_n is the only one, therefore, requiring any adjustment and this is readily done in the following manner:

Differentiating general equation (6) with respect to x , we have

$$\frac{dy_n}{dx} = 2A_n x + B_n \quad (7)$$

which represents the slope at the wpc corresponding to x , and which at normal wpc is equal in value to the constant B_n . Hence, if x' , corresponding to a chosen wpc basis, is found (the value of x' being determined by the substitution of log new basis in equation 1a) and this value be put for x in the above differential equation, we obtain for the slope at the new normal wpc a value

$$B'_n = 2A_n x' + B_n.$$

Therefore, the general equation on the new basis is

$$y'_n = A_n x^2 + (2A_n x' + B_n)x + C' \quad (8)$$

or,

$$y'_n = A_n x^2 + B'_n x + C'. \quad (9)$$

To apply this method of reduction to a particular problem, suppose 1.10 wpc, which is now used as a basis in modern practice, be assumed as normal. The substitution of 0.04139, i. e., log 1.10, in equation 1a gives $x' = 0.01895 = \log 1.0448$, the voltage

ratio corresponding to 1.10 wpc. Substituting in general equation (8) this value of x' , the values of A_n and B_n as taken from Table 1 (for $n=1, 2, 3$, and 4 , respectively), and $\log 1.10$ for C' , we have the following fundamental equations based on the new wpc, the conditional relation among the various quantities being that $x=y'_2=y'_3=y'_4=\log 1=0$ when $y'_1=\log 1.10=0.04139$.

TABLE 2

$$y'_1 = 0.918x^2 - 1.974x + 0.04139 \quad (1')$$

$$y'_2 = -0.946x^2 + 3.556x \quad (2')$$

$$y'_3 = -0.028x^2 + 1.582x \quad (3')$$

$$y'_4 = -0.028x^2 + 0.582x \quad (4')$$

(b) REDUCTION OF KNOWN VALUES

If Y_n is the value of any variable on a basis of 1.20 wpc and Y'_n the corresponding value on any other basis, it is evident, on comparing equations (6) and (9) that

$$\begin{aligned} \log \left(\frac{Y'_n}{Y_n} \right) &= y'_n - y_n = (B'_n - B_n)x + (C' - C) \\ &= 2A_n x' \cdot x + (C' - C) \end{aligned} \quad (10)$$

C' and C being $=0$ except when $n=1$.

Hence, if a curve, or table, of values of the variables Y_n is given, other curves, or tables, of values based on any chosen wpc may be derived at once by applying the antilogarithm of the second member of the equation (10) as a multiplying factor to the given values of Y_n . This method of reduction is exemplified in the Appendix (p. 525).

5. EXAMPLES ILLUSTRATING USE OF THE EQUATIONS

The first step in the solution of every problem by the present method is to determine from the observed values of voltage, candlepower, and wpc the corresponding values at normal efficiency (1.20 wpc).¹⁰ This is done by substituting the values of $\log$ observed wpc in equations 1a and 5a, obtaining from 1a the $\log$ of the ratio of the observed voltage to the voltage corresponding to normal wpc, and from 5a the $\log$ of the ratio of the observed candlepower to the candlepower corresponding to normal. The numeri-

¹⁰ This is the normal wpc used throughout the remainder of the paper.

cal values of voltage and candlepower at normal are obtained by dividing the observed values by the ratios just found. The value of watts at normal equals the product of normal candlepower by 1.20.

As an example to illustrate the use of the equations, let us take the observed values corresponding to the first and second voltages of lamp No. 2658, as given in Table 5, *vis.*,

1	65.0 volts,	6.64 cp.,	3.694 wpc.
2	70.7 "	9.28 "	3.021 "

Substituting in equation 1a the logs of these two values of wpc, in succession, we obtain values for normal voltage as follows:

$$\begin{aligned} 1. \log. \text{ voltage ratio} &= 1.09490 - 1.0439 \sqrt{1.02073 + 0.56750} \\ &= 1.09490 - 1.31557 = 9.77933 - 10. \end{aligned}$$

Or voltage ratio = 0.6016 = 60.16 per cent.

That is, 65.0 volts = 60.16 per cent of normal voltage.

Therefore, normal voltage = $65 \div 0.6016 = 108.04$.

$$\begin{aligned} 2. \log. \text{ voltage ratio} &= 1.09490 - 1.0439 \sqrt{1.02073 + 0.48015} \\ &= 9.81602 - 10. \end{aligned}$$

Or voltage ratio = 0.6546 = 65.46 per cent.

Therefore, normal voltage = $70.7 \div 0.6546 = 108.00$.

Now, substituting the values of the logs of the two values of wpc in equation 5a we obtain values for normal candlepower as follows:

$$\begin{aligned} 1. \log \text{ cp ratio} &= 1.74682 - 1.5878 \sqrt{1.02073 + 0.56750} - 1.031 \times 0.56750 \\ &= 1.74682 - 2.00101 - 0.58510 \\ &= 9.16071 - 10. \end{aligned}$$

Or cp ratio = 14.478 per cent.

Therefore, normal cp = $6.64 \div 0.14478 = 45.87$.

$$\begin{aligned} 2. \log \text{ cp ratio} &= 1.74682 - 1.5878 \sqrt{1.02073 + 0.48015} - 1.031 \times 0.48015 \\ &= 9.30658 - 10. \end{aligned}$$

Or cp ratio = 20.256 per cent.

Therefore, normal cp = $9.28 \div 0.20256 = 45.81$.

The means of these results give the following normal values: 108.02 volts, 45.84 candles, and 55.01 watts ($= 45.84 \times 1.20$). With the above value of voltage (108.02) as basis, computed values for all the variables corresponding to any voltage ratio to normal are found by substituting the log of this ratio in equations 1-4. Values for this lamp corresponding to 65 volts and 70.7 volts are computed as follows. The ratios of these voltages to mean normal (108.02) are 0.6017 and 0.6545, respectively. Substituting the log of these ratios in equation 2, we have

$$\begin{aligned} 1. \log \text{ cp ratio} &= -0.946 (9.77938 - 10)^2 + 3.592 (9.77938 - 10) \\ &= -0.04604 - 0.79247 = -0.83851 \\ &= 9.16149 - 10. \end{aligned}$$

Or cp ratio = 0.14504 = 14.504 per cent.

Therefore, computed cp at 65 volts = $45.84 \times 0.14504 = 6.65$.

$$\begin{aligned} 2. \log \text{ cp ratio} &= -0.946 (9.81591 - 10)^2 + 3.592 (9.81591 - 10) \\ &= -0.03206 - 0.66126 = -0.69332 \\ &= 9.30668 - 10. \end{aligned}$$

Or cp ratio = 20.262 per cent.

Therefore, computed cp at 70.7 volts = $45.84 \times 0.20262 = 9.29$.

These examples are sufficient to show the method of solution. Although the equations are simple and easy to handle, their use involves comparatively long and tedious computations.

6. TABLES OF CHARACTERISTIC RELATIONS

In order to avoid the computations just referred to, a set of tables (19-22) has been calculated from which, with the aid of an ordinary slide rule, the various factors may be read off directly.

It should be stated that the constants as given in the equations of Table 1 do not include as many figures as were actually used in computing the tables of characteristic relations (Tables 19 to 22), but the differences, when differences occur, between the tabulated values and those obtained by means of the equations of Table 1 are, in all cases, so small as to be entirely negligible.

As these tables will be employed, instead of the equations, in what follows, a brief explanation of their use is given here.

Normal values for voltage and candlepower are obtained from the double Table 19 which takes the place of equations 1a and 5a. Observed wpc in steps of 0.1 and intermediate steps of 0.01 are given, respectively, at the top and left margin of the table, and corresponding to these, in the body of the table, are given percentage factors by which observed values of voltage and candlepower, respectively, are to be multiplied to reduce them to values they would have at normal efficiency. These percentage factors are the reciprocals of those which are obtained in a similar reduction by means of equations 1a and 5a. In other words, the equations referred to give *divisors*, while Table 19 gives *multipliers* to be applied to the observed values to reduce them to normal. The table was thus constructed in order to make it consistent with the other three tables, the figures in the body of each table being used as multipliers in every case when per cent values are given.

Having obtained the value for normal candlepower, the value for normal watts is derived by multiplying by 1.20. Knowing the normal values for all the variables, the values corresponding to any percentage of normal volts may then be read from one of the other tables depending upon the variable considered. Practical use of the tables is made in the following section.

VIII. COMPARISON OF COMPUTED AND OBSERVED VALUES

1. METHOD OF DERIVING COMPUTED VALUES

In order to show the method of using the tables in computing values of the several variables, which are later compared with the observed values, computations are made by this method and use of data obtained on lamp No. 2658 are here continued. In Table 19, corresponding to the last seven values of observed wpc, the following percentage factors are found:

No.	Observed wpc	Percentage factors	
		Voltage	Candlepower
1	1.921	125.13	228.4
2	1.754	120.03	195.1
3	1.556	113.44	158.4
4	1.402	107.88	131.8
5	1.274	102.96	111.2
6	1.204	100.16	100.6
7	1.118	96.51	88.08

Applying these factors to the corresponding values of observed voltage and candlepower, respectively, we obtain the following values for normal voltage and normal candlepower, respectively:

TABLE 3

No.	Observed volts	Percentage factor	Normal volts	Observed cp	Percentage factor	Normal cp
1	86.3	$\times 125.13$	-107.99	20.06	$\times 228.4$	-45.82
2	90.0	$\times 120.03$	-108.03	23.49	$\times 195.1$	-45.83
3	95.0	$\times 113.44$	-107.77	28.84	$\times 158.4$	-45.68
4	100.0	$\times 107.88$	-107.88	34.74	$\times 131.8$	-45.80
5	105.0	$\times 102.96$	-108.11	41.28	$\times 111.2$	-45.90
6	108.0	$\times 100.16$	-108.17	45.67	$\times 100.6$	-45.94
7	112.0	$\times 96.51$	-108.09	52.12	$\times 88.08$	-45.91
Mean			-108.01	Mean		-45.84
Av. dev.			-0.10%	Av. dev.		-0.15%

Normal watts— $45.84 \times 1.20 = 55.01$

Therefore the mean normal values for this lamp are: 108.01 volts, 45.84 candles, 55.01 watts.

It will be noticed that the mean normal values for this lamp, as found (p. 499) by the equations from two observed values at and near color match with 4-wpc carbon standards, are identical with those found here from seven observed values. While identical results are not to be expected, the above results show that agreement to about 0.2 per cent in candlepower and 0.1 per cent in voltage on the average would be obtained by using any single set of observed values as basis.

The results of a similar computation on lamp No. 2660 are as follows:

TABLE 4

Observed volts	Normal volts	Normal candles
86.4	107.59	45.35
90.0	107.60	45.34
95.0	107.54	45.35
100.0	107.59	45.38
105.0	107.77	45.56
108.0	107.96	45.64
111.5	107.46	45.31
Means	107.65	45.42
Av. dev.	0.12%	0.23%

Normal watts = $45.42 \times 1.20 = 54.50$

With 108.01 and 107.65, respectively, as the values of normal volts for the two lamps considered, computed values for candlepower, watts, and watts per candle at each observed voltage are obtained from Tables 20, 21, and 22, respectively. For example, the computed values for lamp No. 2658 at 65.0 volts are found as follows:

Since $65.0 = 60.18$ per cent of 108.01 volts, we find in the tables corresponding to this per cent volts the following values:

From Table 22, 3.690 actual wpc, the computed value at 65 volts.

From Table 20, 14.52 per cent candles.

- From Table 21, 44.620 per cent watts.

$$45.84 \times 0.1452 = 6.66, \text{ computed cp at 65 volts.}$$

$$55.01 \times 0.44620 = 24.55, \text{ computed watts at 65 volts.}$$

In this manner computed values corresponding to all the observed voltages are obtained. If the above values are found by means of the equations, the particular ones used are 1, 2, and 3.

2. TABLES OF COMPUTED AND OBSERVED VALUES

TABLE 5

Comparison of Computed and Observed Values

Lamp No. B. S. 2658

Volts	Candles		Watts		Watts per candle	
	Computed	Observed	Computed	Observed	Computed	Observed
65.0	6.66	6.64	24.55	24.53	3.690	3.694
70.7	9.30	9.28	28.07	28.04	3.020	3.021
75.0	11.71	11.76	30.83	30.81	2.634	2.620
80.0	15.03	15.01	34.17	34.15	2.273	2.275
82.0	16.52	16.56	35.53	35.52	2.151	2.145
86.3	20.06	20.06	38.54	38.53	1.921	1.921
90.0	23.49	23.49	41.20	41.19	1.754	1.754
95.0	28.71	28.84	44.88	44.88	1.564	1.556
100.0	34.67	34.74	48.69	48.70	1.404	1.402
105.0	41.40	41.28	52.60	52.61	1.271	1.274
108.0	45.82	45.67	55.00	55.01	1.200	1.204
112.0	52.21	52.12	58.27	58.29	1.116	1.118
	Av. dev., 0.23%		0.04%		0.19%	

Lamp No. B. S. 2660

Volts	Candles		Watts		Watts per candle	
	Computed	Observed	Computed	Observed	Computed	Observed
65.0	6.68	6.67	24.45	24.43	3.661	3.662
70.9	9.43	9.38	28.08	28.06	2.977	2.992
75.0	11.75	11.78	30.71	30.68	2.614	2.605
80.0	15.08	15.05	34.03	34.01	2.257	2.260
82.0	16.57	16.56	35.39	35.37	2.136	2.136
86.4	20.21	20.22	38.46	38.44	1.903	1.901
90.0	23.56	23.59	41.03	41.02	1.742	1.739
95.0	28.81	28.83	44.71	44.70	1.553	1.550
100.0	34.77	34.82	48.49	48.50	1.395	1.393
105.0	41.53	41.41	52.39	52.42	1.262	1.266
108.0	45.96	45.71	54.78	54.79	1.192	1.199
111.5	51.53	51.69	57.62	57.63	1.119	1.115
	Av. dev., 0.23%		0.05%		0.24%	

TABLE 6
Comparison of Computed and Observed Values
Mean of the Group of Seven Lamps

Volts	Candles		Deviation in per cent observed from computed value
	Computed	Observed	
65.0	6.63	6.62	-0.15
70.6	9.18	9.16	-.22
75.0	11.66	11.70	+.34
80.0	14.96	14.98	+.13
82.0	16.45	16.44	-.06
86.5	20.13	20.17	+.20
90.0	23.39	23.41	+.09
95.0	28.61	28.67	+.21
100.0	34.55	34.62	+.20
105.0	41.27	41.20	-.17
108.0	45.68	45.43	-.55
111.8	51.72	51.84	+.21
			Mean... .21%

It should be stated that every lamp of the group was measured at all the voltages given in column 1 of the table with the exception of the second, sixth, and last voltages. These are the means of voltages of the individual lamps, the differences from the mean in every case being less than half a volt. Likewise, the corresponding values of computed and observed candlepower at these voltages are the means of the values for the individual lamps.

3. A SECOND METHOD OF COMPUTING CANDLEPOWER

Another method of computing candlepower values is based on the assumption that computed watts equal observed watts. After obtaining values of voltage and candlepower at normal efficiency the voltage ratios are determined and wpc is read directly from Table 22. Then computed candlepower equals observed watts divided by computed wpc. This method is illustrated also by the use of lamp No. 2658, observed values being taken from Table 5.

TABLE 7

Voltage	Voltage ratios	1 Watts com- puted from Table 21	2 Watts deter- mined from observations of current and voltage	3 Wpc com- puted from Table 22	4 Candles (Col. 2÷Col. 3)	5 Observed candles
65.0	60.18	24.55	24.53	3.690	6.65	6.64
70.7	65.46	28.07	28.04	3.020	9.30	9.28
75.0	69.44	30.83	30.81	2.634	11.71	11.76
80.0	74.07	34.17	34.15	2.273	15.03	15.01
82.0	75.92	35.53	35.52	2.151	16.52	16.56
86.3	79.90	38.54	38.53	1.921	20.06	20.06
90.0	83.33	41.20	41.19	1.754	23.49	23.49
95.0	87.95	44.88	44.88	1.564	28.70	28.84
100.0	92.58	48.69	48.70	1.404	34.68	34.74
105.0	97.21	52.60	52.61	1.271	41.39	41.28
108.0	99.99	55.00	55.01	1.200	45.83	45.67
112.0	103.69	58.27	58.29	1.116	52.21	52.12
		Av. dev. 0.04%		0.22%		

It is seen from the above that the computed watts are of a degree of accuracy sufficiently high that we may employ the values determined from the observations, computing wpc by Table 22, and from the two obtain candlepower by division, *i. e.*, $cp = W \div wpc$. Consequently, Tables 21 and 22 are the only ones which need to be used in adjustments of this kind.

IX. FURTHER VERIFICATION OF THE EQUATIONS

1. APPLICATION TO A GROUP OF DRAWN-WIRE LAMPS OF RECENT MANUFACTURE

Although the lamps used in the determination of the constants of the equations were operated at voltages corresponding to efficiencies no higher than 1.1 wpc (because of their value as standards), the results obtained seemed to justify extrapolation to 0.7 wpc. This value was chosen as a limit because it is often used in life testing of tungsten lamps. However, there arose an opportunity to verify the extrapolated values by a group of lamps submitted for test over this range.

These lamps were manufactured early in 1914 and were not intended for standard purposes. Though there was a slight variation in current, they were remarkably steady for commercial lamps, especially at higher voltages. The computed and observed candlepower values are given in Table 8.

TABLE 8

Comparison of Computed and Observed Values. Group of Seven 40-Watt Drawn Wire Lamps

Volts	Candles		Deviation in per cent observed from computed value
	Computed	Observed	
96	18.26	18.20	-0.33
104	24.51	24.48	-.12
112	32.05	32.15	+.31
120	40.97	41.07	+.24
128	51.37	51.46	+.18
136	63.33	63.48	+.24
144	76.91	76.71	-.26
Wpc range .16 to .72			Mean .24

The maximum deviation of observed from computed candlepower values of a single lamp of this group at one voltage point was 0.56 per cent.

A comparison of the deviations in Tables 6 and 8 (96 volts in the latter corresponding approximately, in wpc, to 95 volts in the former) shows that the voltage-candlepower curve fits the observed values with practically the same degree of accuracy throughout the whole range from 3.7 to 0.7 wpc, and that the + and - deviations are about equal in number.

In order to test fully the accuracy of equation 4, Table 1, as applied to these lamps, the following method was used in obtaining ampere readings on three lamps of the group:

A ballast lamp of 40-watt size was set to a desired voltage, and this voltage was applied suddenly to the lamp under test while rotating approximately 120 rpm.

The test lamp, still rotating, was then thrown out of circuit, the next voltage being determined and applied in the same manner, and so on through all of the voltages. On changing over from ballast to test lamp a small adjustment of voltage (not exceeding 0.2 per cent) was necessary, since the resistances of test and ballast lamps were not quite equal.

Previous measurements had been made as follows:

The lamps while rotating were kept continuously in circuit and the voltages given applied in regular order ascending and descending by adjusting resistance, thus causing the filament to burn at all temperatures included in the voltage range.

Results on one lamp are given in Table 9. The differences on the other lamps were of about the same magnitude.

TABLE 9
Current by Up and Down Method

Volts	Ampere		
	Up	Down	Mean
72	0.26200	0.26248	0.26224
80	.27905	.27940	.27922
88	.29527	.29556	.29542
96	.31083	.31103	.31093
104	.32574	.32599	.32586
112	.34022	.34035	.34028
120	.35413	.35430	.35422
128	.36781	.36782	.36782
136	.38083	.38087	.38085
144	.39365	.39368	.39366

Because of differences between up and down readings at voltages below 112, the method of direct voltage application described above was employed at each voltage from 72 to 112, inclusive, the order of application and observed ampere values being as shown in Table 10.

TABLE 10
Current, Direct Voltage Application Method

Volts	Ampere	Mean ampere	Mean ampere from up and down method
72	0.26231	0.26229	0.26224
112	.34025	.34023	.34028
80	.27924	.27920	.27922
96	.31092	.31090	.31093
88	.29538	.29536	.29542
104	.32582	.32582	.32586
112	.34021		
72	.26227		
104	.32581		
96	.31087		
80	.27915		
88	.29533		

The up and down method had shown values which were very close to those obtained from equation 4 between 112 and 144 volts, but at the lower voltages the residuals were of greater magnitude. The probability of these residuals being greater is indicated by increasing deviations from the mean as the lower voltages are reached. That the method of direct voltage application obviates this difficulty is shown in the following table, in which observed values of current from 72 to 112 volts are those found by this method.

TABLE 11
Comparison of Computed and Observed Values of Current
MEAN OF THREE 40-WATT LAMPS.

Volts	Ampere		Deviation of observed from computed values
	Computed	Observed	
72	0.26183	0.26176	0.00007
80	.27874	.27865	.00009
88	.29481	.29478	.00003
96	.31028	.31027	.00001
104	.32522	.32516	.00006
112	.33956	.33956	.00000
120	.35346	.35346	.00000
128	.36696	.36696	.00000
136	.38007	.38001	.00006
144	.39281	.39280	.00001
Average			.011%

2. APPLICATION TO "GETTER" LAMPS OF VARIOUS SIZES AND MANUFACTURE

The following are lamps of recent manufacture with "getter" material placed on the anchor wires. The filaments were each a single piece of drawn wire mounted on an arbor having five top anchors in some lamps and six in the others.

TABLE 12

Size of lamp	Volts	Candles		Deviation, per cent observed from computed value
		Computed	Observed	
25-watt	88	8.49	8.50	+0.12
	99	13.18	13.14	— .30
	110	19.37	19.37	.00
	121	27.22	27.11	— .41
	Wpc 1.97 to 1.02			Mean .21
40-watt	88	15.34	15.29	—0.33
	99	23.74	23.78	+ .17
	110	34.73	34.78	+ .14
	121	48.63	48.68	+ .10
	Wpc 1.80 to 0.94			Mean .14
60-watt	88	22.44	22.43	—0.05
	99	34.71	34.75	+ .12
	110	50.78	50.82	+ .08
	121	71.09	71.12	+ .04
	Wpc 1.78 to 0.93			Mean .07
100-watt	88	40.34	40.41	+0.17
	99	62.21	62.20	— .02
	110	90.74	90.49	— .28
	121	126.70	126.80	+ .08
	Wpc 1.66 to 0.88			Mean .14

X. USE OF CHARACTERISTIC EQUATIONS IN STANDARDIZING LAMPS

1. LAMPS STANDARDIZED FOR VOLTAGE AT A SPECIFIED CANDLE-POWER

The following illustrates the application of the characteristic equations in standardizing work. The lamps considered were of recent manufacture and were to be standardized as follows:

Lamp No.	Size	Required
1 and 2	25-watt	Volts for 20 candles
3 and 4	40-watt	Volts for 34 candles
5, 6, and 7	60-watt	Volts for 52 candles

The lamps were photometered at five voltages corresponding to the following and against the standards mentioned: (1) At color match with 4-wpc carbon standards; (2) at color match with 1.5-wpc tungsten standards; (3) at two voltages corresponding as nearly as possible to, but on either side of, the required candlepowers, these observations involving color difference with tungsten standards; (4) at color match with tungsten standards whose candlepower values are known through a wide range in voltage, this group including three of the lamps first investigated and three lamps calibrated as working standards in terms of the original group.

The observed values of candlepower and the values of wpc obtained from observed values of voltage and amperes are given in Table 13. Values obtained by the third method (see above) are not given in this table, as they involved measurements at two voltages, one above and the other below the candlepower values required.

TABLE 13
Observed Values

Lamp No.	First method			Second method			Fourth method		
	Volts	Cp	Wpc	Volts	Cp	Wpc	Volts	Cp	Wpc
1	68.7	3.83	3.006	94.0	12.66	1.508	106.8	20.04	1.158
2	69.6	3.87	3.001	96.0	13.15	1.474	107.9	20.00	1.166
3	68.5	6.31	3.036	95.0	21.98	1.467	107.2	34.15	1.144
4	68.2	6.17	3.077	95.0	21.87	1.473	107.3	34.11	1.144
5	68.5	8.94	3.069	95.0	31.10	1.485	109.6	52.20	1.109
6	70.8	9.19	3.071	97.3	31.12	1.506	112.1	52.04	1.128
7	70.8	9.20	3.060	97.6	31.14	1.508	112.3	51.66	1.136

From these observed values for each lamp the voltage for the candlepower required was computed, the value obtained for each being as given in the following table:

TABLE 14
Computed Voltage for Required Candlepower

Lamp No.	First method	Second method	Third method	Fourth method	Means
1	106.7	106.65	106.75	106.8	106.7
2	107.7	107.75	107.9	107.9	107.8
1	107.2	107.1	107.2	107.1	107.2
4	107.3	107.3	107.25	107.2	107.3
5	109.5	109.5	109.55	109.5	109.5
6	112.2	112.1	112.15	112.1	112.1
7	112.3	112.4	112.3	112.5	112.4
Means	109.0	109.0	109.0	109.0	109.0

In Table 15 the observed candlepower values at the voltages corresponding to color match with tungsten standards (see Table 13) are compared with the values obtained by computation from observed values at carbon color.

TABLE 15

Lamp No.	Computed cp	Observed cp	Deviation in per cent observed from computed value
1	12.63	12.66	+0.24
2	13.17	13.15	— .15
3	21.92	21.98	+ .27
4	21.87	21.87	.00
5	31.14	31.10	— .13
6	30.95	31.12	+ .55
7	31.32	31.14	— .57
Means	23.29	23.29	.27

It should be noted that the above lamps were not adjusted to a mean of 23.29 cp, but that the mean of the seven lamps is *actually identical*. This agreement is undoubtedly accidental, as a deviation of at least 0.1 per cent would be expected from a consideration of the mean deviation.

2. LAMPS STANDARDIZED AT GIVEN VOLTAGE BY COMPUTATION FROM VALUES OBSERVED AT COLOR MATCH WITH 4-WPC CARBON STANDARDS

Table 16 illustrates what may be accomplished by computation of candlepower from values determined at a single voltage. These lamps are 60-watt Osram standards (sintered filament), which were measured about two years ago by the Bureau directly in terms of the 4-wpc primary carbon standards, with which they were matched in color by the use of calibrated blue glass screens. These lamps had been previously measured at the National Physical Laboratory, England, in terms of a corresponding group of carbon standards. In both laboratories all measurements were made with the lamps operating at 102.0 volts, corresponding to about 1.5 wpc.

In order to determine how well the equations apply, the lamps were remeasured a short time ago, not at 1.5 wpc, but at color match with 4-wpc carbon standards. At this color their efficiency was about 3.1 wpc, the corresponding voltages of the various lamps being approximately 71. From the values thus obtained those given in column (a) of the table were computed. The values in columns (b) and (c) are, respectively, the certified values of the laboratory indicated.

TABLE 16

Lamp No.	Candles			Deviations in per cent	
	(a) Computed values	(b) B. S. observed values	(c) N. P. L. observed values	(b-a)	(c-a)
57-l	31.9	32.0	31.95	+0.31	+0.16
57-j	27.7	27.85	27.7	+ .54	± .00
57-k	32.85	32.85	32.85	± .00	± .00
57-l	32.45	32.35	32.35	- .31	- .31
57-m	32.25	32.05	32.1	- .62	- .47
57-n	31.75	31.55	31.5	- .63	- .79
Means	31.48	31.44	31.41	.40	.29

Evidently, measurements at color match with either carbon or tungsten standards will suffice to determine the values for candle-

power; further, values of candlepower or voltage at any intermediate point can be computed from the color match observations with no sacrifice in precision, the great advantage being the elimination of personal errors due to color difference.

However, the following points should receive careful attention in this connection: (1) In adjusting the voltage of tungsten lamps for color match with carbon standards great care should be exercised, because if a color match is not really obtained, two observers of like color perception may introduce errors which do not counterbalance even though their observations may appear consistent and conclusive; (2) candlepower values of the smaller sizes of lamps being low, small differences in distance from the test lamps for photometric balance result in considerable differences in observed candlepower values, so that determinations at this point should be made with the highest degree of accuracy attainable, and all confusing features should be eliminated.

XI. REDUCTION OF THE GENERAL EQUATION TO OTHER FORMS

1. EXPONENTIAL FORM

General equation (6) may be readily changed to the form $y = x^u$, which is frequently used in factory and laboratory practice. If we assume Y_n , X , and c as the values of which y_n , x , and C are the logs, then (6) may be written in the form,

$$Y_n = cX^{A_n x + B_n} \quad (11)$$

This becomes evident when logs are taken of both members of equation (11). We then have

$$\log Y_n = A_n (\log X)^2 + B_n (\log X) + \log c$$

or

$$y_n = A_n x^2 + B_n x + C$$

Now, if we assume $c = 1$, C becomes 0, and equation (11) reduces to

$$Y_n = X^{A_n x + B_n} \equiv X^{u_n} \quad (12)$$

where $u_n (= A_n x + B_n)$ is an exponent which may be applied to the voltage ratio, to obtain the corresponding ratios of all the

other variables, wpc included, normal values being at 1.20 wpc. On any other wpc basis this exponent, in accordance with the nomenclature in equation (9), has the value $u_n = A_n x + B'_n$.

With the constants A_n and B'_n known for different normal bases, it is a simple matter to evaluate u_n for any value of x , and to construct a family of curves from which at any observed wpc may be read the proper exponent to apply to any ratio of the observed voltage to obtain the corresponding ratios of the other variables. A family of curves for u_2 , the voltage-candle-power exponent, and another for u_4 , the voltage-current exponent, constructed in this manner, are shown in Figures 1 and 2, respectively. These two families of curves are sufficient for the determination of all values of u_n because the voltage-wattage exponent $u_3 = u_4 + 1$, and the voltage-wpc exponent $u_1 = u_2 - u_3$.

2. DIFFERENTIAL FORM

General equation (9), which is based on a voltage ratio corresponding to any chosen wpc, by differentiation reduces to

$$\frac{dy_n}{dx} = 2A_n x + B'_n \quad (13)$$

which at normal

$$= B'_n \quad (14)$$

For a small finite change in voltage this may be written

$$\Delta y_n = B'_n \Delta x$$

or as a close approximation (using the same nomenclature as in the preceding section)

$$\Delta Y_n = B'_n \Delta X$$

it being assumed that the change in $\log Y_n$ is proportional to the change in Y_n itself. Hence, at normal wpc, the constant B'_n may be used as a multiplying factor for corrections of all the other variables through a small range in voltage. For precision work this range can not exceed 2 per cent, since beyond this limit errors greater than 0.2 per cent in candlepower (not negligible in accurate measurement) will result. As B'_n is the value of the exponent u_n at normal ($x=0$), the values appearing on the 100 per cent curves of

Figures 1 and 2 may be used as differential coefficients to apply to voltage change to obtain corresponding changes in the other variables.

Cady,¹⁰ who has investigated the voltage-candlepower relation, gives a table of coefficients based on 1.25 normal wpc. These values are given below in comparison with values of B_n' as determined by equation (14), normal being taken at 1.25 wpc.

TABLE 17
Comparison of Differential Coefficients

Per cent of normal voltage	Coefficients		
	Cady		M. & S.
	Former	New	
60	4.06	4.06	4.028
70	3.91	3.90	3.901
80	3.79	3.77	3.790
85	3.74	3.71	3.758
90	3.69	3.66	3.695
95	3.64	3.60	3.650
100	3.59	3.56	3.608
105	3.54	3.51	3.568
110	3.49	3.46	3.530
115		3.42	3.493
120		3.39	3.458
130		3.32	3.393
140		3.25	3.332

If we take the mean of two coefficients as determined by equation (13), one for $x=0$, the other for $x=x_1$, we obtain $A_n x_1 + B_n'$, which, by last section, is the value of u_n for the voltage ratio, the log of which is x_1 . Hence, with a table of differential coefficients as that given above, the exponent corresponding to any voltage ratio within the limits of the table is at once obtained by taking the mean of the coefficients corresponding to normal and to the given ratio. For example, using values in the last column of the table, the mean of the values at 70 per cent and 100 per cent volts (viz, 3.901 and 3.608) equals 3.754, the exponent corresponding to 70 per cent volts. Compare with this the value read from Figure 1 at 1.25 wpc and 70 per cent volts.

¹⁰ Elec. Rev. and West. Elec., 58, p. 1092; 1911.

Example illustrating the use of exponents (see Figs. 1 and 2):

Given 100 per cent voltage at 1.10 wpc, to find ratios of candlepower, current, wattage, and wpc at 115 per cent voltage.

Solution: At 1.10 wpc and 115 per cent voltage in Figure 1, we find voltage-candlepower exponent $u_2=3.499$, and in Figure 2 voltage-current exponent $u_4=0.5802$. Then, voltage-wattage exponent $u_3=u_4+1=1.5802$, and voltage-wpc exponent $u_1=u_3-u_2=-1.919$. Therefore,

$$\text{candlepower ratio}=(1.15)^{3.499}=1.631=163.1 \text{ per cent.}$$

$$\text{current ratio}=(1.15)^{0.5802}=1.0845=108.45 \text{ per cent.}$$

$$\text{wattage ratio}=(1.15)^{1.5802}=1.2471=124.71 \text{ per cent.}$$

$$\text{wpc ratio}=(1.15)^{-1.919}=0.76476=76.476 \text{ per cent.}$$

$$\text{actual wpc}=1.10 \times .76476=0.8412$$

A check upon these results may be had by reference to p. 525 where the same problem is solved by means of the tables.

Example illustrating the use of differential coefficients (see Figs. 1 and 2):

Given as observed values, volts 104, candles 32.5, and wpc 1.15, to find volts for 34 candles.

Solution: At 1.15 wpc and 100 per cent voltage in Figure 1 we find $u_2=3.575$.

$$Cp=34-32.5=1.5. \quad \text{Since } \frac{dcp}{cp}=3.575 \frac{d\text{volts}}{\text{volts}} \quad dV=\frac{V dcp}{3.575 cp}=\frac{104 \times 1.5}{3.575 \times 32.5}=1.3 \text{ volts.}$$

Hence, voltage for 34 candles $=V+dV=104+1.3=105.3$, the voltage required.

The use of exponents has been described quite fully by Edwards,¹¹ who also gives two families of curves similar to those shown in Figs. 1 and 2. As a method of reduction the use of exponents is convenient in certain cases, but it requires the use of a table of logarithms, or an exponential slide rule, auxiliary to the curves, and at best the method is merely a special application of the equations of Table 1.

Curves of this kind could, of course, be drawn for any two variables chosen, but all would be based on the equations just referred to. Such curves are useful principally in computations based on one observed value, considered as normal, and of necessity assumed on the characteristic curve.

The more general method described in this paper determines the characteristic curve which most nearly approaches any desired number of observed values, none of which may fall exactly on the curve. Further, reduction to normal values from each of several observations furnishes a valuable preliminary

¹¹ General Electric Review, 17, p. 283; 1914.

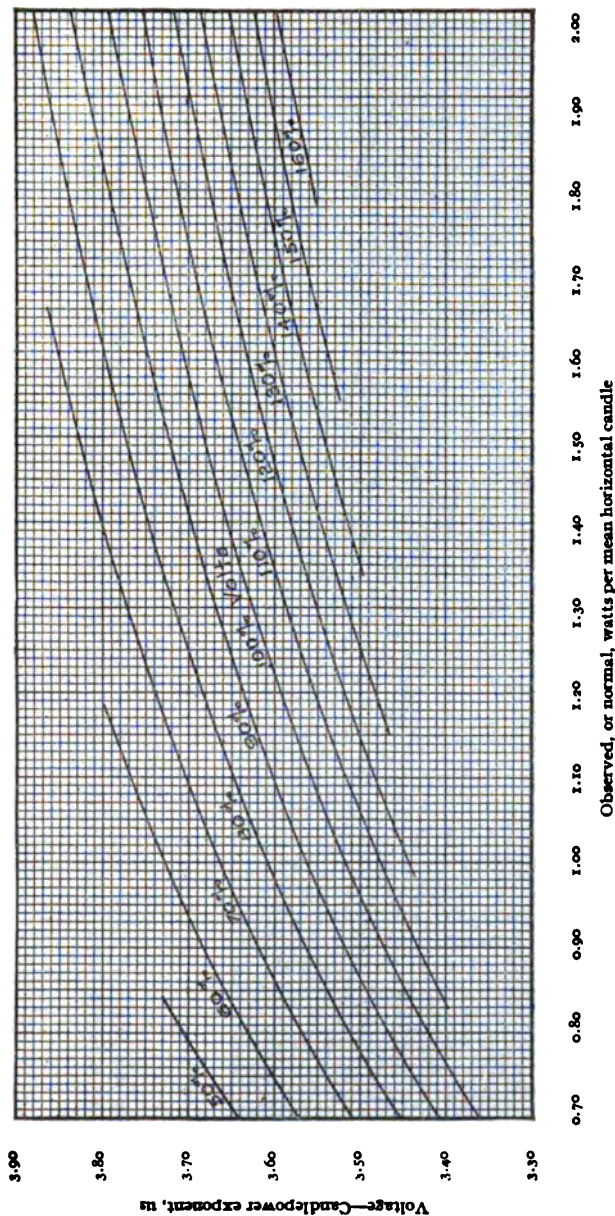


FIG. 1.—From this family of curves may be read, at any observed or normal w_{pc} and per cent of the corresponding voltage, the exponent u_3 which, when applied to the voltage ratio, gives the corresponding candlepower ratio. See example page 516

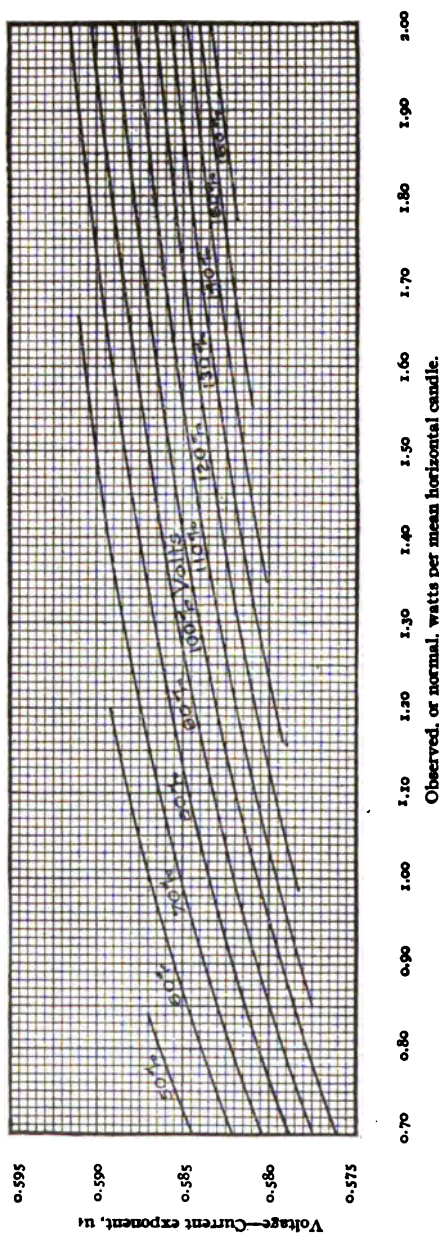


FIG. 2.—From this family of curves may be read, at any observed or normal wpc and per cent of the corresponding voltage, the exponent u , which, when applied to the voltage ratio, gives the corresponding current ratio. See example, page 510

check upon the accuracy of the observations. The problem of reducing observations at any given wpc to values they would have at any other wpc can certainly be most simply solved by the use of the factors read directly from Table 19. (See problem 3, p. 524.)

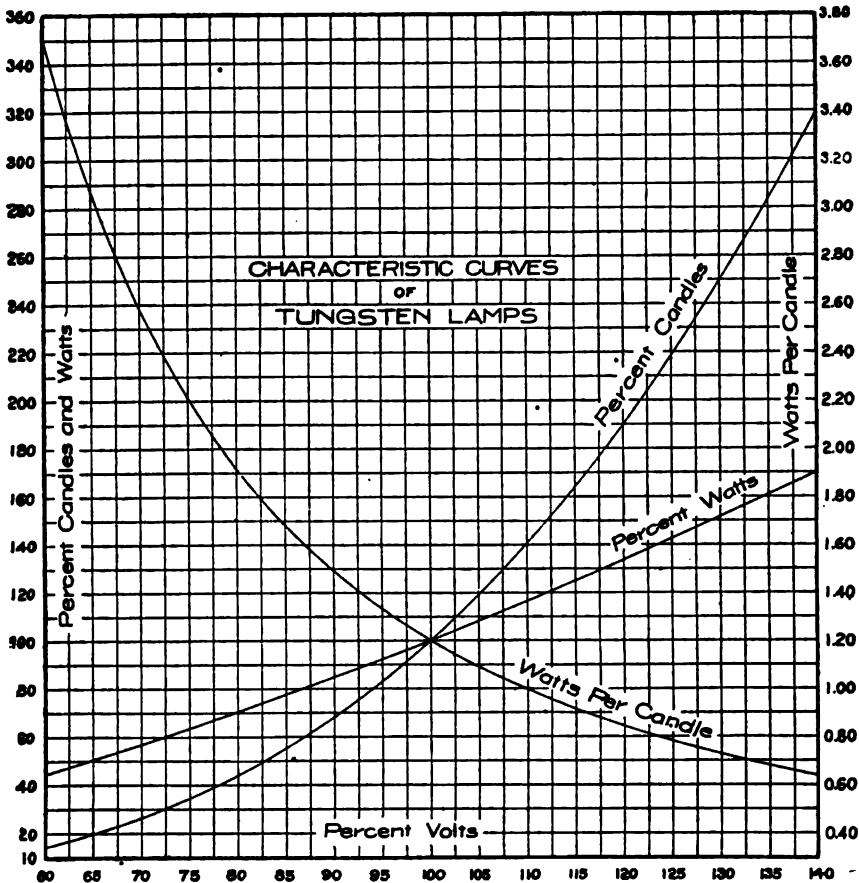


FIG. 3.—Characteristic curves of 100-130-volt vacuum tungsten filament lamps of sizes 25 to 100 watts for the range included between 0.7 and 3.7 wpc, 100 per cent values being at 1.20 wpc

Any derived method based on the fundamental equations of Table 1 can, of course, be made to give results of the same degree of accuracy as those obtained by substitution in the equations themselves. For example, a family of curves of percentage values

could be drawn, each curve being designated by the normal wpc on which it is based. If curves are to be employed, this method would appear to be the most direct, and ordinary sizes of plotting paper could be used, if the range in wpc is not too great, or the data could be divided into sections, each with its own family of curves.

XII. SUMMARY.

The results found in this investigation show that for 100 to 130 volt vacuum tungsten lamps of the ordinary sizes an equation of the form $y_n = A_n x^2 + B_n x + C$ expresses the voltage-candlepower and the voltage-wpc relations to well within 0.3 per cent, and the voltage-wattage relation to well within 0.05 per cent of the observed values over the whole range investigated, viz, from 0.7 wpc to 3.3 wpc, the latter limit extending somewhat beyond the wpc corresponding to color match with 4-wpc carbon lamps.

It is therefore possible, after carefully standardizing a tungsten lamp at color match with the 4-wpc carbon primary standards which maintain the international candle unit, to calculate with a high degree of precision its candlepower, voltage, and current at any desired wpc (or color) within the range mentioned. In this manner groups of standards at different values of wpc may be established in terms of the primary standards without a single measurement made with a color difference.

Further, any standardized tungsten lamp of the size and voltage investigated, together with the set of tables appended, is virtually a standard for use at any wpc (or color) within the range above specified, because its candlepower and current at that color can be completely determined from a knowledge of the corresponding observed voltage. By this method of standardizing lamps, all measurements are made at color match without the use of color screens, which may be entirely discarded, except in so far as they may be of use as auxiliaries in making check measurements.

Although the fundamental equations as given and the tables derived from them are computed on a basis of 1.20 wpc, they are

readily reduced to any other desired basis by any one of several different methods which are fully described.

It is shown that, from the general equation given above, the more important equations heretofore employed may be derived. Curves used in other methods are constructed and the limitations of their use are discussed.

The reduction to normal values, which is the foundation of all computations by the method outlined in this paper, seems to be the simplest and most direct, as it does not directly involve the use of exponents, differentials, or other terms of mathematics beyond those of simple arithmetic.

The wpc employed throughout the paper is watts per mean horizontal candle. Variations in reduction factor among lamps of the same size, or among lamps of different sizes, have not been of sufficient magnitude to affect relative values.

If the relation of life to any one of the variables is known its relation to any other variable may be readily expressed by substitution in the fundamental equations.

As to the effects of a radical change in filament material on lamp characteristics, no prediction is made.

The investigation is being extended to include the gas-filled tungsten lamp, and the results, though yet incomplete, indicate that, provided due consideration is given to certain new variables introduced by this type, the same equations, with little, if any, change in the constants, apply to this lamp also.

The authors are under obligations to their collaborators in the laboratory for assistance in the photometric measurements, especially to Mr. D. H. Tuck; and to Mr. H. B. Sinelnick, who also drew the curves and checked most of the computations.

WASHINGTON, October 10, 1914.

XIV. TABLES OF CHARACTERISTIC RELATIONS

1. EXPLANATION OF USE OF TABLES

The first step in the solution of every problem involving characteristic equations is to determine from the observed values of voltage, candlepower, and wpc the corresponding values at normal efficiency, which for these tables was chosen at 1.20 wpc.

This is done by reference to Table 19, in which observed wpc in steps of 0.1 and intermediate steps of 0.01 are given at the top and left margin, respectively. In the body of the table under "volts" and "cp," respectively, are given the corresponding percentage factors by which the observed voltage and observed candlepower, respectively, are to be multiplied to reduce them to normal values. Normal wattage is found by multiplying normal candlepower by 1.20.

For example, if the observed values are 110 volts, 25 candles, 1.35 wpc, the corresponding normal values are found as follows: Corresponding to 1.35 wpc, find 106.0 under volts and 123.3 under cp. Then, $110 \times 1.060 = 116.6$ volts, $25 \times 1.233 = 30.82$ candles, and $30.82 \times 1.20 = 36.98$ watts, these being the normal values.

With these values known, we are in a position to read from one of the other three tables (viz, 20-22) values corresponding to any desired percentage value of any one of the variables given.

The simplest problem is when values corresponding to a given voltage are required, because all three tables are arranged for voltage considered as the independent variable, and the other variables are given in the body of the table.

For example, assuming the normal values just found, suppose values for candlepower, wattage, and wpc corresponding to 125 volts are required. The voltage ratio $= 125 \div 1.166 = 107.2$ per cent. Corresponding to 107.2 per cent volts in Tables 20, 21, and 22, find 128.1 per cent cp, 111.63 per cent watts, and 1.045 actual wpc, respectively. The numerical values corresponding to the two percentage values are found by multiplying each by the corresponding normal value as follows:

$1.281 \times 30.82 = 39.49$ candles, and $1.1163 \times 36.98 = 41.28$ watts.

Hence the corresponding values of all the variables are 125.0 volts, 39.48 candles, 41.28 watts, and 1.045 wpc.

As a second problem, suppose that the values of voltage, wattage, and wpc, corresponding to 20 candles, are required, the

same normal values being assumed. This candlepower value is $20 \div 30.82 = 64.9$ per cent of normal. From 64.9 per cent cp in the body of Table 20 find the corresponding voltage per cent at the top and margin—that is, $88.0 + (2.14 \div 2.67) = 88.8$ per cent volts. With this value known, find 82.846 per cent watts in Table 21 and 1.532 actual wpc in Table 22. Multiplying percentage values by corresponding normal values, we have $0.888 \times 116.6 = 103.5$ volts, and $0.82846 \times 36.98 = 30.64$ watts. The variables are therefore 20.0 candles, 103.5 volts, 30.64 watts, and 1.532 wpc.

In the same manner values for all the variables corresponding to a given value of wattage or of wpc may be found also.

A third problem of importance to the testing laboratory involves the reduction of voltage, candlepower, and wattage from observed values to values they would have at some given wpc. (For example, a wpc at which the lamps are to be run on life test.) The calculation of voltage is the one of most importance, the other variables being usually neglected in life-test calculations.

Example: Given 110 volts, 88 candles, 1.05 wpc; required volts, candles, and watts at 0.7 wpc.

Solution: In Table 19 find at 1.05 wpc 93.49 per cent volts and 78.66 per cent candles, and at 0.7 wpc 75.26 per cent volts and 37.23 per cent candles. Then at 0.7 wpc

$$\text{volts} = \frac{110 \times 93.49}{75.26} = 136.6$$

$$\text{candles} = \frac{88 \times 78.66}{37.23} = 185.93$$

$$\text{watts} = 185.93 \times 0.7 = 130.15$$

2. REDUCTION OF VALUES TO A WPC BASIS OTHER THAN 1.20

If some other wpc than 1.20 be chosen as normal, tables of values can be readily determined from these tables by any of the three following methods:

(a) Suppose, for example, that 1.10 wpc is chosen as normal. Corresponding to 1.10 in Table 22 find 104.48 per cent volts. Corresponding to 104.48 per cent volts in Tables 20 and 21 find 116.9 per cent cp and 107.18 per cent watts, respectively. Therefore, the values in the present tables corresponding to normal in the new tables are as follows: 104.48 per cent volts, 116.9 per cent cp, 107.18 per cent watts, and 1.10 actual wpc.

Now, suppose, for example, that values at 115.0 per cent volts on the new basis are required. Voltage ratio is then $115.0 \times 1.0448 = 120.15$ per cent. Corresponding to 120.15 per cent volts in Tables 20, 21, and 22 find 190.7 per cent cp, 133.66 per cent watts, and 0.8412 actual wpc, respectively.

Hence, corresponding to 115.0 per cent volts, we have for the new tables:

$$\begin{aligned} 120.15 \div 1.0448 &= 115.0 \text{ per cent volts,} \\ 190.7 \div 1.169 &= 163.1 \text{ per cent candles,} \\ 133.66 \div 1.0718 &= 124.71 \text{ per cent watts,} \\ &\text{and } 0.8412 = \text{actual wpc.} \end{aligned}$$

In the same manner, values corresponding to other percentage values of voltage may be found, and a complete set of tables corresponding to Tables 20, 21, and 22, on the new basis, may be constructed.

Values for Table 19 are obtained by dividing the tabulated values of the factors designated "volts" by 0.9573 and those designated "cp" by 0.8554, these being the values at 1.10 wpc. For example, the tabulated values of "volts" and "cp" at 1.00 wpc in Table 19 are 91.17 and 72.00, respectively. Values for the new table are then

$$\frac{91.17}{0.9573} = 95.24 \text{ "volts" and } \frac{72.00}{0.8554} = 84.17 \text{ "cp."}$$

(b) Values corresponding to each point in Tables 20, 21, and 22 need not necessarily be computed as given above. A simple method is to compute values at points, say, 5 or 10 per cent apart in voltage (for example, 80, 85, 90, 95, etc.) and taking differences between the values obtained and those given in the tables. Then, with per cent volts as ordinates and differences as abscissas, a smooth curve may be drawn through the points found, and from it the difference at any per cent volts may be read. These differences added to the tabulated values give values for the new tables.

(c) The ratio of the values based on any normal wpc to the values given in Tables 20 to 22, inclusive, may be accurately computed from equation (10), page 498. Designating this ratio by R_n and its logarithm by r_n , equation (10) becomes

$$r_n = 2A_n x' \cdot x + (C' - C) \equiv K_n x + L,$$

C' and C being = 0 except when $n = 1$, x representing any voltage ratio on the new normal wpc basis, and x' the voltage ratio on

the 1.20-wpc basis corresponding to the new normal wpc. The following table gives values for R_n for a normal 1.10-wpc basis:

TABLE 18

Factors by Which Tabulated Values May Be Multiplied to Obtain Corresponding Values for a Normal 1.10 Wpc Basis

Per cent volts	R_n Table 20	R_n Table 21	R_n Table 22
60	1.019	1.0005	0.9004
70	1.013	1.0004	.9053
80	1.008	1.0002	.9095
90	1.004	1.0001	.9133
100	1.000	1.0000	.9167
110	0.9966	0.99989	.9197
120	.9935	.99982	.9225
125	.9920	.99977	.9238

From a smooth curve drawn through the above values of per cent volts as ordinates and R_n as abscissas, the values of R_n may be read for any per cent volts, and the new tables may be quickly and accurately constructed.

Values for Table 19 are most easily obtained by method (a) first outlined above.

3. TABLES OF CHARACTERISTIC RELATIONS

TABLE 19

Table of percentage multiplying factors for reducing observed values of voltage and observed values of candlepower at known wpc to values they would have at 1.20 wpc. Voltage factors are indicated by "Volts"; candlepower factors by "Cp."

Example: Given as observed values, 112.0 volts, 16.0 candles, 1.450 wpc, to find volts and candles at 1.20 wpc.

Solution: Corresponding to 1.450 wpc find 109.7, the voltage percentage multiplier, and 139.9, the candlepower percentage multiplier. The values corresponding to 1.20 wpc are, therefore, $112.0 \times 1.097 = 122.86$ volts, and $16.0 \times 1.399 = 22.38$ candles.

Obs. wpc	0.70				0.80				0.90			
	Volts	D.L.	Cp	D.L.	Volts	D.L.	Cp	D.L.	Volts	D.L.	Cp	D.L.
0.00	73.26		37.23		81.01		47.79		86.29		59.40	
.01	73.86	0.60	38.24	1.01	81.56	0.55	48.90	1.11	86.79	0.50	60.61	1.21
.02	76.45	.59	39.26	1.02	82.10	.54	50.03	1.13	87.29	.50	61.84	1.23
.03	77.04	.59	40.29	1.03	82.64	.54	51.16	1.13	87.79	.50	63.07	1.23
.04	77.62	.58	41.33	1.04	83.17	.53	52.31	1.15	88.28	.49	64.32	1.25
.05	78.20	.58	42.38	1.05	83.70	.53	53.47	1.16	88.77	.49	65.57	1.25
.06	78.77	.57	43.44	1.06	84.23	.53	54.64	1.17	89.26	.49	66.84	1.27
.07	79.34	.57	44.51	1.07	84.75	.52	55.81	1.17	89.74	.48	68.11	1.27
.08	79.90	.56	45.60	1.09	85.27	.52	57.00	1.19	90.22	.48	69.40	1.29
.09	80.46	.56	46.69	1.09	85.78	.51	58.19	1.19	90.70	.48	70.69	1.29
.10	81.01	.55	47.79	1.10	86.29	.51	59.40	1.21	91.17	.47	72.00	1.31

Obs. wpc	1.00				1.10				1.20			
	Volts	D.L.	Cp	D.L.	Volts	D.L.	Cp	D.L.	Volts	D.L.	Cp	D.L.
0.00	91.17		72.00		95.73		85.54		100.0		100.0	
.01	91.64	0.47	73.31	1.31	96.17	0.44	86.95	1.41	100.4	0.4	101.5	1.5
.02	92.11	.47	74.63	1.32	96.60	.43	88.36	1.41	100.8	.4	103.0	1.5
.03	92.57	.46	75.96	1.33	97.04	.44	89.78	1.42	101.2	.4	104.5	1.5
.04	93.03	.46	77.31	1.35	97.47	.43	91.22	1.44	101.6	.4	106.0	1.5
.05	93.49	.45	78.66	1.35	97.90	.43	92.66	1.44	102.0	.4	107.6	1.6
.06	93.94	.45	80.02	1.36	98.32	.42	94.11	1.45	102.4	.4	109.1	1.5
.07	94.39	.45	81.38	1.36	98.75	.43	95.57	1.46	102.8	.4	110.6	1.5
.08	94.84	.45	82.76	1.38	99.17	.42	97.04	1.47	103.2	.4	112.2	1.6
.09	95.29	.44	84.14	1.38	99.59	.42	98.51	1.47	103.6	.4	113.8	1.6
.10	95.73		85.54	1.40	100.00	.41	100.00	1.49	104.0	.4	115.3	1.5

TABLE 19—Continued

Obs. wpc	1.30				1.40				1.50			
	Volts	Dif.	Cp	Dif.	Volts	Dif.	Cp	Dif.	Volts	Dif.	Cp	Dif.
0.00	104.0		115.3		107.8		131.5		111.5		148.5	
.01	104.4	0.4	116.9	1.6	108.2	0.4	133.1	1.6	111.8	0.3	150.2	1.7
.02	104.8	.4	118.5	1.6	108.6	.4	134.8	1.7	112.2	.4	152.0	1.8
.03	105.2	.4	120.1	1.6	109.0	.4	136.5	1.7	112.5	.3	153.7	1.7
.04	105.6	.4	121.7	1.6	109.3	.3	138.2	1.7	112.9	.4	155.5	1.8
.05	106.0	.4	123.3	1.6	109.7	.4	139.9	1.7	113.2	.3	157.3	1.8
.06	106.4	.4	124.9	1.6	110.0	.3	141.6	1.7	113.6	.4	159.1	1.8
.07	106.8	.4	126.5	1.6	110.4	.4	143.3	1.7	113.9	.3	160.9	1.8
.08	107.1	.3	128.2	1.7	110.8	.4	145.0	1.7	114.3	.4	162.7	1.8
.09	107.5	.4	129.8	1.6	111.1	.3	146.8	1.8	114.6	.3	164.5	1.8
.10	107.8	.3	131.5	1.7	111.5	.4	148.5	1.7	115.0	.4	166.3	1.8

Obs. wpc	1.60				1.70				1.80			
	Volts	Dif.	Cp	Dif.	Volts	Dif.	Cp	Dif.	Volts	Dif.	Cp	Dif.
0.00	115.0		166.3		118.3		184.8		121.4		204.1	
.01	115.3	0.3	168.1	1.8	118.6	0.3	186.7	1.9	121.8	0.4	206.1	2.0
.02	115.6	.3	169.9	1.8	118.9	.3	188.6	1.9	122.1	.3	208.0	1.9
.03	116.0	.4	171.8	1.9	119.2	.3	190.5	1.9	122.4	.3	210.0	2.0
.04	116.3	.3	173.6	1.8	119.6	.4	192.4	1.9	122.7	.3	212.0	2.0
.05	116.6	.3	175.4	1.8	119.9	.3	194.4	2.0	123.0	.3	214.0	2.0
.06	117.0	.4	177.3	1.9	120.2	.3	196.3	1.9	123.3	.3	216.0	2.0
.07	117.3	.3	179.2	1.9	120.5	.3	198.2	1.9	123.6	.3	218.0	2.0
.08	117.6	.3	181.0	1.8	120.8	.3	200.2	2.0	123.9	.3	220.0	2.0
.09	117.9	.3	182.9	1.9	121.1	.3	202.2	2.0	124.2	.3	222.1	2.1
.10	118.3	.4	184.8	1.9	121.4	.3	204.1	1.9	124.5	.3	224.1	2.0

TABLE 19—Continued

Obs. wpc	1.90				2.00				2.10			
	Volts	Dit.	Cp	Dit.	Volts	Dit.	Cp	Dit.	Volts	Dit.	Cp	Dit.
0.00	124.5		224.1		127.4		244.9		130.3		266.3	
.01	124.8	0.3	226.2	2.1	127.7	0.3	247.0	2.1	130.6	0.3	268.5	2.2
.02	125.1	.3	228.2	2.0	128.0	.3	249.2	2.2	130.8	.2	270.7	2.2
.03	125.4	.3	230.3	2.1	128.3	.3	251.3	2.1	131.1	.3	272.9	2.2
.04	125.7	.3	232.3	2.0	128.6	.3	253.5	2.2	131.4	.3	275.1	2.2
.05	126.0	.3	234.4	2.1	128.9	.3	255.6	2.1	131.6	.2	277.4	2.3
.06	126.3	.3	236.5	2.1	129.1	.2	257.8	2.2	131.9	.3	279.6	2.2
.07	126.6	.3	238.6	2.1	129.4	.3	259.9	2.1	132.2	.3	281.8	2.2
.08	126.9	.3	240.7	2.1	129.7	.3	262.0	2.2	132.5	.2	284.0	2.2
.09	127.2	.2	242.8	2.1	130.0	.3	264.2	2.1	132.7	.3	286.2	2.2
.10	127.4		244.9		130.3		266.3		133.0		288.4	

	2.20				2.30				2.40			
	Volts	Dit.	Cp	Dit.	Volts	Dit.	Cp	Dit.	Volts	Dit.	Cp	Dit.
0.00	133.0		288.4		135.7		311.1		138.3		334.5	
.01	133.3	0.3	290.6	2.2	135.9	0.2	313.4	2.3	138.5	0.2	336.9	2.4
.02	133.6	.3	292.9	2.3	136.2	.3	315.8	2.4	138.8	.3	339.3	2.4
.03	133.8	.2	295.2	2.3	136.5	.3	318.2	2.4	139.0	.2	341.7	2.4
.04	134.1	.3	297.5	2.3	136.7	.2	320.5	2.3	139.3	.3	344.1	2.4
.05	134.4	.3	299.8	2.3	137.0	.3	322.8	2.3	139.5	.2	346.5	2.4
.06	134.6	.2	302.0	2.2	137.2	.2	325.2	2.4	139.8	.3	348.9	2.4
.07	134.9	.3	304.3	2.3	137.5	.3	327.5	2.3	140.0	.2	351.3	2.4
.08	135.2	.3	306.6	2.3	137.8	.3	329.8	2.3	140.3	.3	353.7	2.4
.09	135.4	.2	308.9	2.3	138.0	.2	332.2	2.4	140.5	.2	356.1	2.4
.10	135.7	.3	311.1	2.2	138.3	.3	334.5	2.3	140.8	.3	358.5	2.4

TABLE 19—Continued

Obs. wpc	2.50				2.60				2.70			
	Volts	DtL	Cp	DtL	Volts	DtL	Cp	DtL	Volts	DtL	Cp	DtL
0.00	140.8		358.5		143.2		383.2		145.6		408.5	
.01	141.0	0.2	361.0	2.5	143.4	0.2	385.7	2.5	145.8	0.2	411.1	2.6
.02	141.3	.3	363.5	2.5	143.7	.3	388.2	2.5	146.0	.2	413.6	2.5
.03	141.5	.2	365.9	2.4	143.9	.2	390.8	2.6	146.3	.3	416.2	2.6
.04	141.7	.2	368.4	2.5	144.1	.2	393.3	2.5	146.5	.2	418.8	2.6
.05	142.0	.3	370.9	2.5	144.4	.3	395.8	2.5	146.7	.2	421.4	2.6
.06	142.2	.2	373.3	2.4	144.6	.2	398.4	2.6	147.0	.3	424.0	2.6
.07	142.5	.3	375.8	2.5	144.9	.3	400.9	2.5	147.2	.2	426.6	2.6
.08	142.7	.2	378.3	2.5	145.1	.2	403.4	2.5	147.4	.2	429.2	2.6
.09	143.0	.3	380.7	2.4	145.3	.2	405.9	2.5	147.6	.2	431.8	2.6
.10	143.2	.2	383.2	2.5	145.6	.3	408.5	2.6	147.9	.3	434.4	2.6
	2.80				2.90				3.00			
0.00	147.9		434.4		150.1		460.8		152.3		487.8	
.01	148.1	0.2	437.0	2.6	150.3	0.2	463.5	2.7	152.6	0.3	490.6	2.8
.02	148.3	.2	439.6	2.6	150.6	.3	466.2	2.7	152.8	.2	493.3	2.7
.03	148.6	.3	442.3	2.7	150.8	.2	468.9	2.7	153.0	.2	496.0	2.7
.04	148.8	.2	444.9	2.6	151.0	.2	471.6	2.7	153.2	.2	498.8	2.8
.05	149.0	.2	447.6	2.7	151.2	.2	474.3	2.7	153.4	.2	501.5	2.7
.06	149.2	.2	450.2	2.6	151.4	.2	477.0	2.7	153.6	.2	504.3	2.8
.07	149.4	.2	452.8	2.6	151.7	.3	479.7	2.7	153.8	.2	507.0	2.7
.08	149.7	.3	455.5	2.7	151.9	.2	482.4	2.7	154.0	.2	509.8	2.8
.09	149.9	.2	458.1	2.6	152.1	.2	485.1	2.7	154.2	.2	512.6	2.8
.10	150.1	.2	460.8	2.7	152.3	.2	487.8	2.7	154.4	.2	515.4	2.8

TABLE 19—Continued

Obs. wpc	3.10				3.20			
	Volts	Dil.	Cp	Dil.	Volts	Dil.	Cp	Dil.
0.00	154.4	0.2	515.4	2.7	156.5	0.2	543.5	2.8
.01	154.6	.2	518.1	2.8	156.7	.2	546.3	2.9
.02	154.8	.2	520.9	2.8	156.9	.2	549.2	2.8
.03	155.0	.3	523.7	2.8	157.1	.2	552.0	2.9
.04	155.3	.2	526.5	2.8	157.3	.3	554.9	2.9
.05	155.5	.2	529.3	2.9	157.6	.2	557.8	2.9
.06	155.7	.2	532.2	2.8	157.8	.2	560.7	2.8
.07	155.9	.2	535.0	2.9	158.0	.2	563.5	2.9
.08	156.1	.2	537.9	2.8	158.2	.2	566.4	2.9
.09	156.3	.2	540.7	2.8	158.4	.2	569.3	2.9
.10	156.5		543.5		158.6		572.2	

TABLE 20

Table for determining values of candlepower corresponding to observed values of voltage, when the values of both candlepower and voltage at 1.20 wpc are known. All values in this table are expressed in per cent.

Example: Given 125.0 volts and 34.0 candles, both at 1.20 wpc, to find candles at 100.0 volts.

Solution: 100.0 volts=80 per cent of 125.0 volts. Corresponding to 80 per cent volts find in the table 43.95 per cent candles. Therefore, candles at 100.0 volts=43.95 per cent of 34.0=14.94.

Obs. volts	60		70		80		90	
	Cp	Dil.	Cp	Dil.	Cp	Dil.	Cp	Dil.
0	14.34		26.35		43.95		68.18	
1	15.32	0.98	27.84	1.49	46.06	2.11	71.01	2.83
2	16.35	1.03	29.39	1.55	48.24	2.18	73.91	2.90
3	17.42	1.07	31.00	1.61	50.48	2.24	76.89	2.98
4	18.54	1.12	32.66	1.66	52.79	2.31	79.94	3.05
5	19.72	1.18	34.39	1.73	55.18	2.39	83.08	3.14
6	20.94	1.22	36.18	1.79	57.63	2.45	86.30	3.22
7	22.22	1.28	38.03	1.85	60.16	2.53	89.60	3.30
8	23.54	1.33	39.94	1.91	62.76	2.60	92.98	3.38
9	24.92	1.38	41.91	1.97	65.43	2.67	96.45	3.47
10	26.35	1.43	43.95	2.04	68.18	2.75	100.00	3.55

Obs. volts	100		110		120		130	
	Cp	Dil.	Cp	Dil.	Cp	Dil.	Cp	Dil.
0	100.0		140.3		189.9		249.5	
1	103.6	3.6	144.8	4.5	195.4	5.5	256.0	6.5
2	107.4	3.8	149.4	4.6	201.0	5.6	262.6	6.6
3	111.2	3.8	154.2	4.8	206.7	5.7	269.4	6.8
4	115.1	3.9	159.0	4.8	212.5	5.8		
5	119.0	3.9	163.9	4.9	218.4	5.9		
6	123.1	4.1	168.9	5.0	224.4	6.0		
7	127.3	4.2	174.0	5.1	230.5	6.1		
8	131.5	4.2	179.2	5.2	236.7	6.2		
9	135.9	4.4	184.5	5.3	243.0	6.3		
10	140.3	4.4	189.9	5.4	249.5	6.5		

TABLE 21

Table for determining values of wattage corresponding to observed values of voltage when the values of both wattage and voltage at 1.20 wpc are known. All values in this table are expressed in per cent.

Example: Given 98.0 watts and 110.0 volts, both at 1.20 wpc, to find watts at 90.2 volts.

Solution: 90.2 volts=82 per cent of 110.0 volts. Corresponding to 82 per cent, find in the table 73.007 per cent watts. Therefore, watts at 90.2 volts=73.007 per cent of 98.0=71.55 watts.

Obs volts	60		70		80		90	
	Watts	DtL	Watts	DtL	Watts	DtL	Watts	DtL
0	44.406		56.772		70.200		84.628	
1	45.593	1.187	58.067	1.295	71.599	1.399	86.123	1.495
2	46.791	1.196	59.374	1.307	73.007	1.408	87.628	1.505
3	48.000	1.209	60.691	1.317	74.426	1.419	89.142	1.514
4	49.220	1.220	62.019	1.328	75.854	1.428	90.666	1.524
5	50.451	1.231	63.357	1.338	77.292	1.438	92.199	1.533
6	51.694	1.243	64.705	1.348	78.740	1.448	93.741	1.542
7	52.947	1.253	66.064	1.359	80.198	1.458	95.292	1.551
8	54.211	1.264	67.432	1.368	81.665	1.467	96.852	1.560
9	55.486	1.275	68.811	1.379	83.142	1.477	98.422	1.570
10	56.772	1.286	70.200	1.389	84.628	1.486	100.000	1.578

Obs volts	100		110		120		130	
	Watts	DtL	Watts	DtL	Watts	DtL	Watts	DtL
0	100.00		116.27		133.40		151.35	
1	101.59	1.59	117.95	1.68	135.16	1.76	153.19	1.84
2	103.19	1.60	119.63	1.68	136.93	1.77	155.04	1.85
3	104.79	1.60	121.32	1.69	138.70	1.77	156.89	1.85
4	106.40	1.61	123.02	1.70	140.49	1.79		
5	108.03	1.63	124.73	1.71	142.28	1.79		
6	109.66	1.63	126.45	1.72	144.08	1.80		
7	111.30	1.64	128.17	1.72	145.88	1.80		
8	112.95	1.65	129.91	1.74	147.70	1.82		
9	114.60	1.65	131.65	1.74	149.52	1.82		
10	116.27	1.67	133.40	1.75	151.35	1.83		

TABLE 22

Table for determining watts per candle corresponding to observed voltage when the latter is expressed in per cent of the voltage at 1.20 wpc.

Example: Given 115.0 volts at 1.20 wpc, to find watts per candle corresponding to 96.6 volts.

Solution: 96.6 volts=84.0 per cent of 115.0 volts. Corresponding to 84 per cent volts, find in the table 1.724, the wpc required.

Obs. volts	60		70		80		90	
	Wpc	DtL	Wpc	DtL	Wpc	DtL	Wpc	DtL
0	3.716		2.585		1.916		1.490	
1	3.571	0.145	2.502	0.083	1.865	0.051	1.456	0.034
2	3.435	.136	2.424	.078	1.816	.049	1.423	.033
3	3.306	.129	2.349	.075	1.769	.047	1.391	.032
4	3.185	.121	2.278	.071	1.724	.045	1.361	.030
5	3.070	.115	2.211	.067	1.681	.043	1.332	.029
6	2.962	.108	2.146	.065	1.640	.041	1.304	.028
7	2.860	.102	2.085	.061	1.600	.040	1.276	.028
8	2.763	.097	2.026	.059	1.562	.038	1.250	.026
9	2.672	.091	1.970	.056	1.525	.037	1.224	.026
10	2.585	.087	1.916	.054	1.490	.035	1.200	.024

Obs. volts	100		110		120		130	
	Wpc	DtL	Wpc	DtL	Wpc	DtL	Wpc	DtL
0	1.200		0.9945		0.8431		0.7280	
1	1.176	0.024	.9773	0.0172	.8301	0.0130	.7182	0.0098
2	1.153	.023	.9606	.0167	.8175	.0126	.7084	.0098
3	1.131	.022	.9443	.0163	.8053	.0122	.6989	.0095
4	1.110	.021	.9286	.0157	.7934	.0119		
5	1.089	.021	.9133	.0153	.7818	.0116		
6	1.069	.020	.8984	.0149	.7705	.0113		
7	1.049	.020	.8840	.0144	.7595	.0110		
8	1.031	.018	.8700	.0140	.7487	.0108		
9	1.012	.019	.8564	.0136	.7382	.0105		
10	0.9945	.0175	.8431	.0133	.7280	.0102		

A VIBRATION ELECTROMETER

By Harvey L. Curtis

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I. INTRODUCTION

The telephone and the vibration galvanometer ¹ have long been used to detect very small alternating currents and voltages. The telephone is very sensitive in the range of frequencies from 500 to 3000 cycles, but has the disadvantage of responding to harmonics as well as to the fundamental. The vibration galvanometers are relatively insensitive to the harmonics, and are much more sensitive at the lower frequencies than is a telephone.

The sensitiveness of an instrument may be defined in terms of the *voltage* which must be applied to give unit deflection, or it may be defined in terms of the *current* which will give unit deflection.² In order that either a telephone or a vibration galvanometer shall be very sensitive to an alternating *current*, it must be con-

¹ The most important types of vibration galvanometers, the range of frequencies for which they are usually used, and the place where they are first described are as follows:

Type	Range (cycles)	Reference.
Rubens.....	50-200	Wied. Ann., 56, p. 27; 1895.
Wien.....	50-1,000	Ann. d. Phys., 209, p. 425; 1901.
Campbell.....	50-1,000	Phil. Mag., [6] 14, p. 494; 1907.
Duddell.....	300-3,000	Phil. Mag., [6] 18, p. 168; 1909.
Drysdale.....	20-200	Electr., 69, p. 939; 1912.

² For a discussion of this, see F. Wenner, A theoretical and experimental study of the vibration galvanometer, this bulletin, 6, p. 347, Reprint 134, 1909.

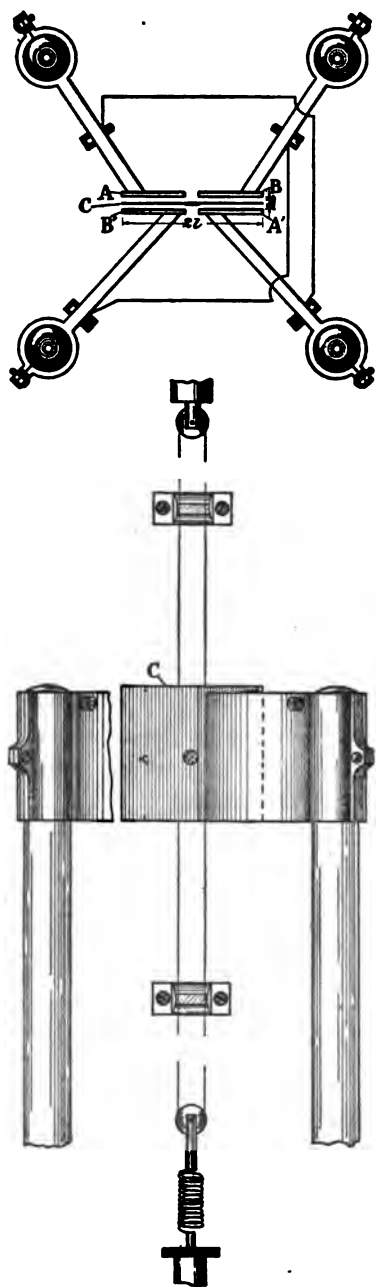


FIG. 1.—Plan and elevation of the vibration electrometer

structed of very fine wire. A limit is soon reached in this direction, due to the difficulties in making and handling very fine wire. A vibration electrometer will detect very much smaller alternating currents than either of the above instruments. Such an instrument has already been described by Greinacher,³ although his description did not appear until after the instrument here described had been constructed. He adapted a Wulf electrometer, using a transformer in connection with the instrument.

The instrument here described is a modification of a quadrant electrometer. The need for it arose in connection with the measurements of very small capacities at low frequencies. By means of it, capacities of the value of a thousandth of a microfarad have been measured at 50 cycles with an accuracy about 10 times greater than can be obtained by any vibration galvanometer in this laboratory. For smaller capacities, the advantage is still greater. However, it is useful only when the impedance of the bridge arms is very high, so that the current which flows through them is very small. Also it can not be used at frequencies much above 100 cycles on account of the moment of inertia of the vane.

³ Phys. Zs., 18, pp. 388, 433; 1912.

As the design is of such form as to make a mathematical treatment of its behavior rather simple, the equations governing its operation have been worked out in some detail. Following this are some experimental results to show the agreement between theory and practice, together with some hints in the practical use of the instrument.

II. DESCRIPTION OF INSTRUMENT

The instrument consists of four metal plates A, A₁, B, and B₁, diagonally opposite plates being connected as shown in Fig. 1. Between these a light aluminum vane C is supported by means of a bifilar suspension. This vane is free to vibrate about a vertical axis. The plates correspond to the quadrants of a quadrant electrometer, while the vane corresponds to the needle. If an electrostatic charge is given to the vane, and an alternating electromotive force is applied to the plates, the vane will be forced to vibrate in the period of the applied electromotive force. If the natural period of the suspended system is identical with the period of the applied electromotive force, then the amplitude of vibration is largely increased. The natural period can be varied by changing the length of the bifilar suspension, by varying the distance between the suspensions, or by altering the tension on the suspensions. When in resonance, the amplitude will depend upon the damping, and as air damping is a large part of the total damping, the whole instrument is placed under a bell jar, from which the air can be exhausted.

III. THEORY OF THE INSTRUMENT

As the instrument is a modification of the quadrant electrometer, the theory will be much the same. However, the form of the instrument is such that calculations are somewhat simplified, and more exact results can be obtained.

The capacity of two rectangular planes inclined at an angle is given by Rosa and Dorsey ⁴ as

$$C = \frac{bl}{4\pi d_1} \left[1 - \frac{1}{2} \frac{d_2 - d_1}{d_1} + \frac{1}{3} \left(\frac{d_2 - d_1}{d_1} \right)^2 - \dots \dots \dots \right]$$

providing edge corrections can be neglected.

⁴ This Bulletin, 8, p. 486, 1907. Reprint No. 65.

Where b is the breadth of the plates, l their length, d_2 the greatest distance between them, and d_1 the least distance.

$$\text{Putting } \sin \theta = \frac{d_2 - d_1}{l}$$

$$C = \frac{bl}{4\pi d_1} \left[1 - \frac{1}{2} \frac{l \sin \theta}{d_1} + \frac{1}{3} \frac{l^2 \sin^2 \theta}{d_1^2} - \dots \dots \dots \right] \quad (1)$$

If d_1 remains constant while d_2 diminishes, it can be shown that formula (1) holds when d_2 becomes less than d_1 , thus making θ negative. Hence we shall drop the subscript to d_1 , writing it d .

If one of the plates vibrates in such a manner that d and l remain constant, while θ is a known function of the time, the capacity at any instant is given by equation (1). While, in this instrument, the condition that d should remain constant is fulfilled only when there is an infinitely small distance between A and B on the one side and A_1 and B_1 on the other, yet the approximation is very close with the distances used.

From Fig. 1 it is seen that there are three insulated conductors $A - A_1$, $B - B_1$, and C , so that six coefficients of capacity are necessary to determine the charges upon the plates when known potentials are applied to them.

If q_1 is the charge upon $A - A_1$ and E_1 its potential

If q_2 is the charge upon $B - B_1$ and E_2 its potential

If q_3 is the charge upon C and E_3 its potential

then

$$\left. \begin{aligned} q_1 &= C_{11}E_1 + C_{12}E_2 + C_{13}E_3 \\ q_2 &= C_{21}E_1 + C_{22}E_2 + C_{23}E_3 \\ q_3 &= C_{31}E_1 + C_{32}E_2 + C_{33}E_3 \end{aligned} \right\} \quad (2)$$

where C_{11} , C_{12} , etc., are the coefficients of capacity between the three systems.

From equation (1), it follows that

$$\left. \begin{aligned} C_{11} &= K_1 + \frac{bl}{2\pi d} \left(1 + \frac{1}{2} \frac{l \sin \theta}{d} + \frac{1}{3} \frac{l^2 \sin^2 \theta}{d^2} + \dots \right) \\ C_{22} &= K_2 + \frac{bl}{2\pi d} \left(1 - \frac{1}{2} \frac{l \sin \theta}{d} + \frac{1}{3} \frac{l^2 \sin^2 \theta}{d^2} - \dots \right) \\ C_{33} &= K_3 + \frac{bl}{\pi d} \left(1 + \frac{1}{3} \frac{l^2 \sin^2 \theta}{d^2} + \dots \right) \\ C_{12} &= -K \\ C_{13} &= -\frac{bl}{2\pi d} \left(1 + \frac{1}{2} \frac{l \sin \theta}{d} + \frac{1}{3} \frac{l^2 \sin^2 \theta}{d^2} + \dots \right) \\ C_{23} &= -\frac{bl}{2\pi d} \left(1 - \frac{1}{2} \frac{l \sin \theta}{d} + \frac{1}{3} \frac{l^2 \sin^2 \theta}{d^2} - \dots \right) \end{aligned} \right\} \quad (3)$$

Where b , l , d , and θ have the values previously given, and K , K_1 , K_2 , and K_3 are constants

If W is the total potential energy of the system at any instant, then

$$W = \frac{1}{2} C_{11} E_1^2 + \frac{1}{2} C_{22} E_2^2 + \frac{1}{2} C_{33} E_3^2 + C_{12} E_1 E_2 + C_{13} E_1 E_3 + C_{23} E_2 E_3 \quad (4)$$

If the torque at an angle θ is M

$$M = \frac{dW}{d\theta}$$

Substituting values from (3) in (4) and taking the derivative.

$$\begin{aligned} M &= \frac{bl}{4\pi d} \left\{ E_1^2 \left(\frac{1}{2} \frac{l \cos \theta}{d} + \frac{2}{3} \frac{l^2 \sin \theta \cos \theta}{d^2} + \dots \right) \right. \\ &\quad + E_2^2 \left(-\frac{1}{2} \frac{l \cos \theta}{d} + \frac{2}{3} \frac{l^2 \sin \theta \cos \theta}{d^2} - \dots \right) \\ &\quad + E_3^2 \left(+\frac{4}{3} \frac{l^2 \sin \theta \cos \theta}{d^2} + \dots \right) \\ &\quad + E_1 E_2 \left(-\frac{l \cos \theta}{d} - \frac{4}{3} \frac{l^2 \sin \theta \cos \theta}{d^2} - \dots \right) \\ &\quad + E_1 E_3 \left(\frac{l \cos \theta}{d} - \frac{4}{3} \frac{l^2 \sin \theta \cos \theta}{d^2} + \dots \right) \left. \right\} \end{aligned}$$

If now $E_1 = -E_2 = E_0 \cos pt$, where E_0 is the maximum value of the alternating electromotive force, p is 2π times its period, and t the time.

$$M = \frac{bl}{4\pi d} \left\{ \frac{4}{3} \frac{l^2 \sin \theta \cos \theta}{d^2} (E_0^2 \cos^2 pt + E_s^2) - \frac{2l \cos \theta}{d} E_0 E_s \cos pt \right\} \quad (5)$$

If θ is small, then for a first approximation, $\sin \theta = \theta$ and $\cos \theta = 1$.

Also if E_s^2 is large relative to E_0 , equation (5) reduces to

$$\begin{aligned} M &= \frac{bl}{4\pi d} \left\{ \frac{4}{3} \frac{E_s^2 l^2 \theta}{d^2} - \frac{2l E_0 E_s}{d} \cos pt \right\} \\ &= \frac{1}{3} \frac{bl^3 E_s^2}{\pi d^3} \theta - \frac{1}{2} \frac{bl^2 E_0 E_s}{\pi d^2} \cos pt \end{aligned} \quad (6)$$

In any system free to move around an axis, the sum of all the torques at any instant must equal zero.

Hence

$$K \frac{d^2 \theta}{dt^2} + D \frac{d\theta}{dt} + V\theta = \frac{1}{3} \frac{bl^3 E_s^2}{\pi d^3} \theta - \frac{1}{2} \frac{bl^2 E_0 E_s}{\pi d^2} \cos pt \quad (7)$$

Where K is the moment of inertia of the rotating system,

D is the damping coefficient,

V is the restoring couple of the suspension,

and θ is the angle of rotation.

The complete solution of this equation is

$$\theta = C_1 e^{(-\alpha + \beta)t} + C_2 e^{(-\alpha - \beta)t} + \delta \cos (pt - \gamma) \quad (8)$$

Where

$$\alpha = \frac{D}{2K}; \quad (9)$$

$$\beta = \frac{1}{2K} \sqrt{D^2 - 4KV + \frac{4}{3} \frac{Kbl^3 E_s^2}{\pi d^3}} \quad (10)$$

$$\delta = \frac{1}{2} \frac{bl^2 E_0 E_s}{\pi d^2 \sqrt{D^2 p^2 + \left(V - \frac{1}{3} \frac{bl^3 E_s^2}{\pi d^3} - Kp^2 \right)^2}} \quad (11)$$

$$\gamma = \tan^{-1} \frac{-Dp}{V - \frac{1}{3} \frac{bl^3 E_s^2}{\pi d^3} - Kp^2} \quad (12)$$

The first two terms of the second member of equation (8) diminish with the time. They are of importance for only a short time after closing or opening the circuit. Hence, if the instrument is kept on closed circuit they may be neglected.

In the use of the instrument we are desirous that the value of δ , which is the amplitude of vibration, should be a maximum for a given value of E_0 . In other words, if the instrument is used on an alternating-current bridge, a slight lack of balance should produce a relatively large vibration of the instrument. An examination of expression (11) shows that for a maximum value of δ , D , the damping coefficient, should be small. This damping is of two parts—the friction and molecular loss in the suspension wires, and the damping due to air friction. In this instrument the air damping is a very large part of the total loss, and this can be greatly diminished by putting the instrument under a bell jar and exhausting the air. However, as will be pointed out later, it may not be desirable to reduce the damping to as low a point as possible.

If the expression (11) is differentiated with respect to E_s , assuming all the other quantities constant, and the result equated to zero, the resulting equation serves to determine the value of E_s which will make δ a maximum. This value of E_s is

$$E_s = \sqrt[4]{K^2 p^4 + (D^2 - 2VK)p^2 + V^2} \sqrt{\frac{3\pi d^3}{bl^3}} \quad (13)$$

In the same way, by differentiating (11) with respect to p , the value of p for a maximum δ is

$$p^2 = \frac{V - \frac{bl^3 E_s^2}{3\pi d^3} - \frac{D^2}{2K}}{K} \quad (14)$$

Hence, we see from (14) that if E_s is increased p is decreased to obtain a maximum value of δ . but V , the restoring couple, must always be larger than

$$\frac{bl^3 E_s^2}{3\pi d^3} + \frac{D^2}{2K}$$

since the frequency must be greater than zero. By substituting (14) in (11) the value of δ , when p is adjusted for a maximum value is

$$\delta_m = \frac{1}{2} \frac{b^2 E_0 E_s \sqrt{K}}{\pi d^2 D \sqrt{V - \frac{b^2 E_s^2}{3\pi d^2} - \frac{D^2}{4K}}} = \frac{b^2 E_0 E_s \sqrt{K}}{2\pi d^2 D \sqrt{K p^2 + \frac{D^2}{4K}}} \quad (15)$$

From this it is seen that an increase of E_s will cause an increase of δ , both by increasing the numerator and decreasing the denominator until $V = \frac{b^2 E_s^2}{3\pi d^2} + \frac{D^2}{4K}$ when δ becomes infinite. Thus, we see that if p and E_s can both be varied, increasing E_s , the voltage on the vane, decreases p the frequency for a maximum amplitude, and this maximum amplitude δ_m increases more rapidly than E_s . If E_s is sufficiently large, $p = 0$ and $\delta_m = \infty$, though as E_s increases p becomes zero before δ_m becomes infinite. Hence when E_s is too large, the vane, if slightly displaced, deflects until it strikes the plates and the electrostatic forces which tend to keep it in this position are greater than the restoring forces of the suspension.

The conditions for maximum amplitude are, therefore, small damping, a large but not excessive voltage on the vane, and the frequency of the applied voltage adjusted until the maximum amplitude is obtained. These conditions are in addition to those which are imposed by the instrument itself, such as the size and mass of the vane, the distance apart of the plates, and the torsional rigidity of the suspension. A discussion of the effect of these would follow the methods already indicated.

Next to securing a large amplitude of vibration for a small electromotive force impressed upon the plates comes the question of sharpness of tuning. It may be that a vibrating instrument will give a very large amplitude for a particular value of the frequency, yet the amplitude will decrease so rapidly with changes in frequency that it is a very difficult instrument with which to work. This is due to the fact that no source of alternating electromotive force is entirely free from fluctuations in frequency.

The sharpness of tuning S may be defined as the reciprocal of the resonance range R , where the resonance range is the difference, in proportional parts, between the frequency for maximum ampli-

tude, p_m , and the frequency $p_{\frac{m}{2}}$ which will reduce the amplitude to one-half of the maximum. Or in symbols

$$S = \frac{1}{R} = \frac{p_m}{p_m - p_{\frac{m}{2}}} \quad (16)$$

If the value of δ given in (11) is put equal to one-half of the maximum value of δ given in (15), and this equation solved for p^2 (which then is $p_{\frac{m}{2}}^2$)

$$p_{\frac{m}{2}}^2 = p_m^2 \pm \frac{D}{2K^2} \sqrt{12K^2 p_m^2 + 3D^2}$$

Therefore

$$p_m - p_{\frac{m}{2}} = \pm \frac{D \sqrt{12K^2 p_m^2 + 3D^2}}{2K^2 (p_m + p_{\frac{m}{2}})}$$

If the resonance range is small relative to $2p_m$, $p_m + p_{\frac{m}{2}} = 2p_m$ approximately.

$$\therefore R = \frac{D \sqrt{12K^2 p_m^2 + 3D^2}}{4K^2 p_m^2} \quad (17)$$

When used as a sensitive instrument D is small relative to Kp_m . Then

$$R = \frac{D \sqrt{3}}{2K p_m}$$

Hence the resonance range is proportional to the damping and inversely proportional to the moment of inertia of the moving system. Stated otherwise, the sharpness of tuning increases as the damping decreases or as the moment of inertia increases. By reference to equation (11) we see that whatever the frequency, a decrease in the damping will increase the amplitude, though it is only in the neighborhood of resonance that this has an appreciable effect.

It may be desirable to know what current is necessary to operate such an instrument. This is somewhat complicated by the fact that the current in the two wires leading to the two plates is not the same at any instant, though the integral value is the same.

The current in the wire leading to $A-A_1$ can be found by differentiating q_1 in equations (2) with respect to the time. In case E_s is large relative to E_0 and hence is large relative to E_1 and E_2 , and to their derivatives when the frequency is low, we have as a first approximation

$$i_1 = \frac{dq_1}{dt} = E_s \frac{dc_{1s}}{dt} = -E_s \frac{bl}{2\pi d} \left(\frac{1}{2} \frac{l}{d} + \frac{2}{3} \frac{l^2 \theta}{d^2} + \dots \right) \frac{d\theta}{dt}$$

As θ is a small quantity, we can neglect the second term of this expression. Then, since $\theta = \delta \cos (pt - \gamma)$, it follows that

$$\frac{d\theta}{dt} = -\delta p \sin (pt - \gamma)$$

and

$$i_1 = E_s \delta p \frac{bl^2}{4\pi d^2} \sin (pt - \gamma) \quad (18)$$

From this we see that δ , the amplitude of vibration of the vane, is directly proportional to the current. If values of δ and γ under the condition that δ is a maximum are substituted in (18),

$$i_1 = \frac{E_s^2 E_0 p_m b^2 l^4 K}{4\pi^2 d^4 (4p_m^2 K^2 + D^2)} \sin pt + \frac{E_s^2 E_0 p_m^2 b^2 l^4 K^2}{2\pi^2 d^4 D (4p_m^2 K^2 + D^2)} \cos pt. \quad (19)$$

From this we see that the in-phase component of the current (the coefficient of $\cos pt$) is inversely proportional to the damping. Hence as the damping is diminished the in-phase current, and therefore the power supplied to the moving system, increases for a given value of the emf., E_0 , impressed on the plates.

The power, P , supplied to the moving system can be obtained from (19) and (15) in the form $P = \frac{\delta_m^2 p_m^2 D}{2}$. This shows that if δ_m is maintained constant, P decreases in the same ratio as D .

Under the assumptions which we have made, the current flowing in the conductor which leads to the plates $B-B_1$ is equal and of opposite sign to the current flowing to the plates $A-A_1$. If the neglected terms are included, this is not the case. This is most easily shown by determining the current that flows in the conductor leading to the vane. This is found from the value of q_s in equation (2) by differentiating with respect to the time. Carrying out this process and substituting values, $i_s = H \sin (2pt - \epsilon)$,

where H and ϵ are constants whose values can be easily evaluated. Since $i_1 + i_2 + i_3 = 0$, it follows that i_1 is not equal to $-i_2$.

The preceding discussion has been based upon the assumption that the instrument is on closed circuit. In actual use the current is changed by adjusting the bridge for which the electrometer is serving as a detecting instrument, and it is desirable to have the deflection reach a steady condition as soon as possible. In order to determine this, it will be necessary to examine the values of α and β in equation 8. If we neglect for the moment the periodic term $\delta \cos (pt - \gamma)$ the remaining portion θ_1 may be written in the form

$$\theta_1 = e^{-\alpha t} (C_1 e^{\beta t} + C_2 e^{-\beta t})$$

By substituting the value of p_m from equation (14) in (12),

$$\beta = \frac{1}{2K} \sqrt{-4p_m^2 K^2 - D^2}$$

Hence β is always imaginary under the condition of maximum deflection. In this case θ_1 is periodic, having an amplitude $Re^{-\alpha t}$ and a period which is nearly equal to p_m when the damping is small. The constant R depends upon the initial conditions and can not be determined except as these are known. The rate at which the amplitude decreases with time depends upon α .

Since $\alpha = \frac{D}{2K}$, the rate at which the exponential term will disappear will increase as the damping, D , increases. To be able to use the instrument satisfactorily, the damping must be large enough so that the deflection will reach its normal value within a few seconds after closing the circuit or making any change which will affect the flow of current through the instrument.

IV. EXPERIMENTAL VERIFICATION OF THE THEORY

The experimental work has been carried on with a view of testing the validity of the formulas developed in the theoretical work. A diagram of the set-up used in this work is shown in Fig. 2. Four condensers, C_1 , C_2 , C_3 , and C_4 , are arranged in the form of a Wheatstone's bridge, C_3 and C_4 being mica condensers of the same

nominal value, while C_1 and C_2 are variable air condensers. A small resistance r is connected in series with the mica condenser having the lowest phase difference and adjusted to make the phase difference of the mica condensers the same. To this is connected an alternating current voltage, whose frequency can be varied over quite wide limits by varying the speed of the generator. The voltage applied to the bridge is measured by a voltmeter V . The midpoints of the bridge are connected to the plates of the vibrating electrometer, while the vane of the instrument is connected to a battery whose voltage can be varied in steps of 40 volts.

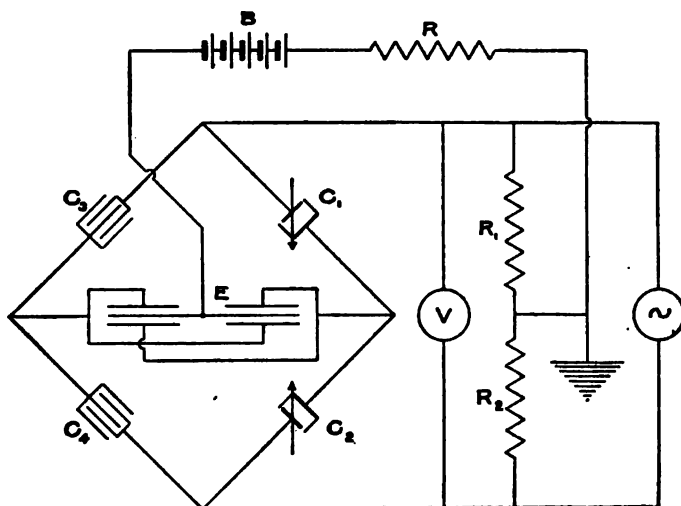


FIG 2.—Diagram of the set-up for testing the vibration electrometer

The opposite pole of the battery is connected to earth through a high resistance R . The value of R must be sufficiently large to prevent reactions between the bridge and the battery, but not so large as to be comparable with the leakage paths from the battery. In this investigation R has been kept at one megohm. The terminals of the bridge are connected to two equal resistances R_1 and R_2 in series, the midpoint of these resistances being grounded. Hence the midpoint of the bridge is also at earth potential at every instant.

Upon the vane of the electrometer there is mounted a small mirror. The image of a lamp filament formed by this mirror is

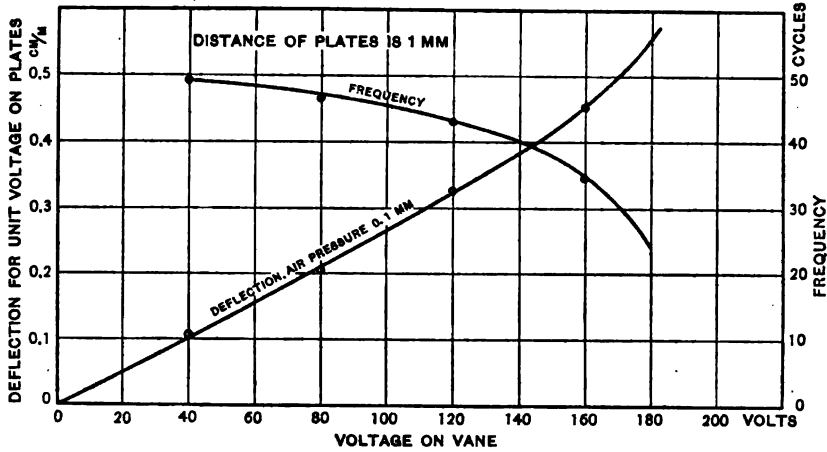


FIG. 3.—Curves showing the effect of voltage on the vane upon the frequency at which resonance occurs and upon the deflection at resonance for one air pressure and for a distance between the plates of 1 mm

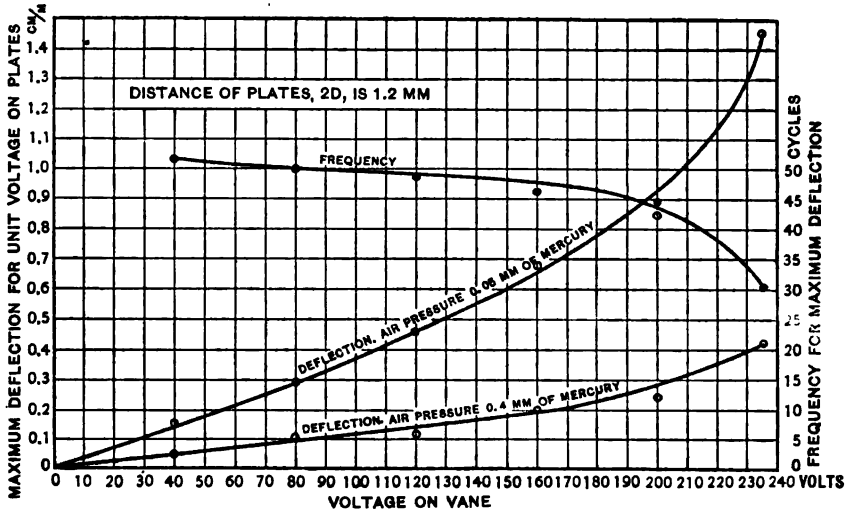


FIG. 4.—Curves showing the effect of voltage on the vane upon the frequency at which resonance occurs and upon the deflection at resonance for different air pressures and for a distance between the plates of 1.2 mm

viewed by a telescope in the eyepiece of which there is a graduated scale. For determining the sensitiveness and sharpness of tuning under any given conditions, C_1 and C_2 are adjusted until a balance is obtained; then C_1 is decreased until at the frequency of maximum sensitiveness the deflection is two divisions of the eyepiece scale. From the values of C_1 , C_2 , and the applied voltage the sensitiveness of the instrument can be computed. Then the frequency is varied on each side of the maximum until the deflection is reduced to one division. This gives the data for computing the sharpness of tuning.

In all of the experiments the size of the vane and of the plates has remained the same, viz, $l = 1$ cm and $b = 2$ cm. The distance, $2d$, between the plates is variable, and in some experiments the effect of varying this distance has been shown. Its value will be given in all cases.

In Fig. 3 is given a curve showing the maximum deflection for unit voltage on the plates with different voltages on the vane (the distance between the plates being 1 mm). In Fig. 4 are exactly similar curves where the distance between the plates is 1.2 mm. The air pressure in the bell jar surrounding the instrument is given for each curve. It will be noted in each case that while the curve is approximately a straight line for low voltages on the vane, yet as the voltage increases a point is reached where the deflection increases rapidly. With a distance of 1 mm between the plates the vane deflected so as to strike the plates when 200 volts were applied. In the discussion of equation (15) it was pointed out that such a condition would be reached. It was also pointed out that, as that condition is approached, the frequency will approach zero. In Figs. 3 and 4 the frequency is also plotted as a function of the voltage on the vane. It will be seen that the frequency begins to decrease markedly at the same time that the sensitiveness begins to increase.

In Fig. 5 are curves showing the sensitiveness with a distance of 2 mm between the plates. In this case the pressures have been reduced much lower than in the preceding cases, thus making the measurements much more difficult. For the range of voltages used the curves are straight lines within the limit of measurement.

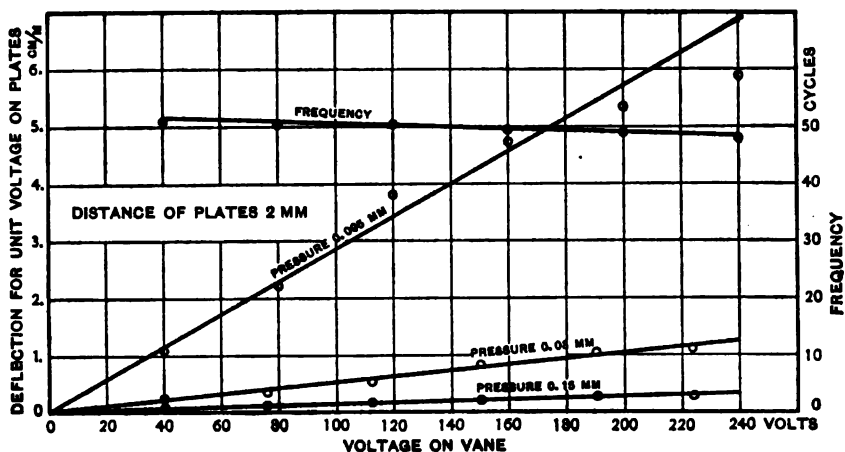


FIG. 5.—Curves showing the effect of voltage on the vane upon the frequency at which resonance occurs and upon the deflection at resonance for different air pressures and for a distance between the plates of 2 mm

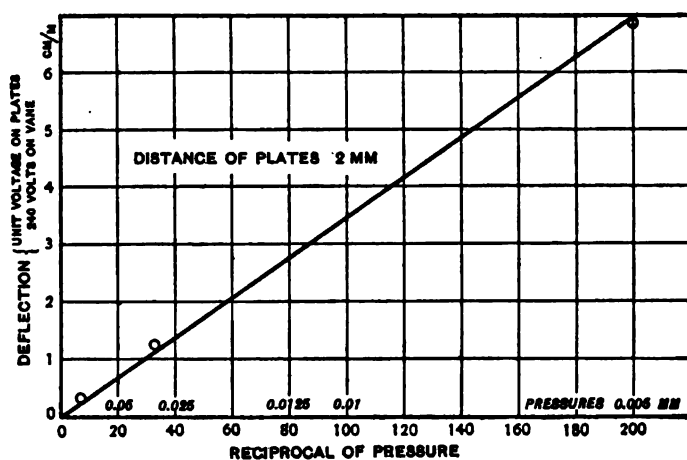


FIG. 6.—Curve showing that the deflection is inversely proportional to the damping

From the mean values of the deflection obtained from the curves of Fig. 5 are obtained values by means of which the curve of Fig. 6 is plotted. We may assume that the air damping of the vane is proportional to the air pressure.⁵ Then when the damping due to the friction of the suspension is comparable to that due to the air, the curve will bend toward the horizontal. As there is no such tendency at a pressure of 0.005 mm of mercury, it is apparent that the damping due to the suspension is exceedingly small. In some preliminary experiments when the friction of the suspension over the bridge was rather large the damping due to the suspension was not negligible. This curve shows experimentally that which is derived theoretically in equation (15), viz, that the maximum amplitude is inversely proportional to the damping.

In equation (17) it is shown from theoretical considerations that the resonance range is proportional to the damping, provided $4K^2p_m^2$ is large relative to D^2 . In Fig. 7 is given a curve showing the experimental relationship found. Within the experimental error the curve is a straight line.

In Fig. 8 are shown curves representing the deflection at different frequencies with different air pressures. It shows in a very marked way the increase in sensitiveness and the decrease in resonance range as the damping decreases.

The current which flows into the instrument can be determined from equation (18) by means of the data given in Fig. 8. From this we find that the current required to give a deflection of 1 cm at a meter's distance is approximately 10^{-9} ampere. As an observer can detect one one-hundredth of this deflection, the current which will produce a noticeable deflection is only 10^{-11} ampere.

V. SUMMARY

An electrostatic instrument, called a vibration electrometer, is described. It is capable of detecting alternating currents of low frequency having a value as small as 10^{-11} ampere. The theory of the instrument is developed mathematically and the conclusions verified by experiment. The important conclusions are as follows:

1. For any given adjustment of the instrument, the frequency at which maximum deflection is obtained depends upon the poten-

⁵ See Hogg, Friction in Gases at Low Pressures. *Phil. Mag.* [6], 19, p 376: 1910.

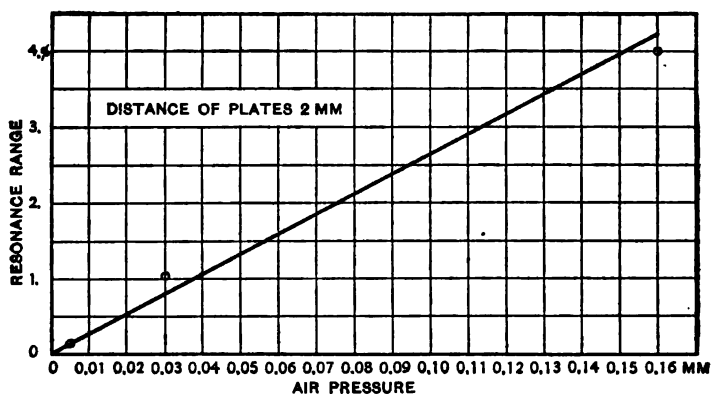


FIG. 7.—Curve showing that the resonance range is proportional to the damping

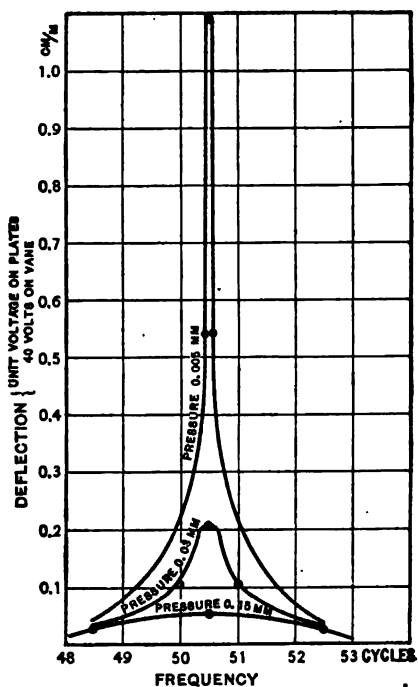


FIG. 8.—Curves showing the increase in sensitiveness and decrease in resonance range as the damping is decreased

tial of the vane. As the potential of the vane is increased, the frequency at which maximum deflection is obtained is decreased.

2. When the voltage on the vane is increased, the deflection for a given voltage on the plates increases more rapidly than the first power of the voltage. The sensitivity can not be increased indefinitely in this way, since the frequency will become zero before the sensitiveness becomes infinite.

3. The deflection is inversely proportional to the damping. It is shown experimentally that the damping due to a well-constructed suspension is exceedingly small.

4. As the damping is decreased, the range of frequencies over which the instrument can be used is greatly diminished. Hence it is not important to decrease the damping beyond a reasonable point.

5. Upon closing the circuit or otherwise changing the current through the electrometer, some time is required before the amplitude of vibration becomes constant. This time will be increased as the damping is decreased.

6. The power required to give unit deflection when the applied emf is in resonance with the instrument decreases in the same ratio as the damping.

WASHINGTON, September 29, 1914.

STUDIES ON THE SILVER VOLTAMETER

By G. A. Hulett and G. W. Vinal

I. INTRODUCTION

At the suggestion of Prof. E. B. Rosa, of the Bureau of Standards, a comparison has been made of the silver voltameters and methods employed at the Bureau of Standards with the voltameters and methods used at Princeton University by Prof. Hulett and his coworkers. In January, 1914, one of the authors (G. W. Vinal) therefore went to Princeton with part of the Bureau of Standards equipment of voltameters.

This work was intended to include a comparison of the methods of preparing the electrolyte, of the porous cups and their manipulation, of the methods of washing and weighing the deposit, and of other details of operation in order to find an explanation for certain differences in conclusions reached and to see whether when the electrolyte was pure and the manipulation the same, the voltameters, which were of different sizes and shapes, would give identical results. In addition, it was planned to study the question of inclusions in the deposit if time permitted.

This program was in the main carried out except for the matter of the inclusions, for which, owing to unexpected developments in some of the other work, there was not sufficient time. It seems worth while to call attention to these new developments at the present time.

Throughout the following discussion the apparatus and methods which have heretofore been used and described by Prof. Hulett and his students are designated as the Princeton apparatus or method. Similarly, also, we shall refer to the Bureau apparatus and methods as previously described in the recent publications of the Bureau of Standards on this subject.

II. COMPARISON OF THE VOLTAMETERS

1. PRELIMINARY WORK

A preliminary comparison of the voltameters was made in four experiments (of which the first is designated as a trial experiment) to determine the relation of the Princeton voltameters with those of the Bureau of Standards. In each case the voltameters were assembled and treated in accordance with the customary procedure. But the electrolyte used in all the voltameters of any experiment was always the same,¹ so that we have a comparison of the voltameters themselves not involving any differences due to the preparation of the silver nitrate. The voltameters were all of the porous-cup variety.²

TABLE 1

Preliminary Comparison of Voltameters

[Nos. 27 and 28 are Bureau of Standards voltameters; I and II are Princeton voltameters]

Date	Cup	Deposit	Mean	Difference, B. S.—Princ.
1914 Feb. 18	27	mg 4103.34	mg 4103.34	
	28	(4102.94)		
	I		4103.12	
	II	4103.12		$\frac{+5.4}{100\ 000}$
Feb. 26	27	4090.84	4090.87	
	28	4090.90		
	I	4090.39	4090.43	
	II	4090.47		$\frac{+10.7}{100\ 000}$
Mar. 7	27	4118.32	4118.34	
	28	4118.36		
	I	4117.54	4117.61	
	II	4117.68		$\frac{+17.7}{100\ 000}$
Mar. 20	27	4094.55	4094.55	
	28	4094.55		
	I	4094.23	4094.23 ₆	
	II	4094.24		$\frac{+7.7}{100\ 000}$
Mean				$\frac{+10.4}{100\ 000}$

¹ This electrolyte was prepared according to the methods of the Bureau of Standards. This Bulletin, 9, p. 524.

² Details of construction of these voltameters are given in Trans. Am. Electrochem. Soc., 12, p. 257; 22, p. 367; and this Bulletin, 9, p. 151.

³ Vacuum dried; all others dried by heating to 160°.

The values are given in Table 1. On the average the deposits in the Bureau voltameters exceeded those in the Princeton voltameters by about 10 parts in 100 000.

A systematic search was now begun for the cause of this difference. In Table 2 we give the physical aspects of the voltameters employed.

Differences in the method of washing the deposits proved to be important and without doubt influenced the results given in Table 1. We shall describe under the heading "Washing the deposits" the experiments which we made in this connection. The essential fact here is that according to the Princeton method the voltameters always stood overnight filled with distilled water, while the Bureau procedure has been to complete the washings of the deposit at once, unless the lateness of the hour made it convenient to allow the cups to remain filled with water overnight. This was a most unexpected result and on examining the matter carefully we have discovered that when water is allowed to stand on silver which has been deposited on platinum a slow and progressive loss of silver takes place. During the interval between closing work for one day and beginning the next the loss is appreciable in amount.

Comparative determinations of the acidity of the electrolyte for the various voltameters before and after the electrolysis showed the following results. These were made according to the method described by Rosa, Vinal, and McDaniel,⁴ except that methyl red was employed as an indicator instead of iodeosine, because it is much more convenient to use and seems to be equally reliable.

TABLE 2

Comparison of the Physical Aspects of the Voltameters

[Nos. 27 and 28 are Bureau of Standards voltameters; I and II are Princeton voltameters. Platinum cathodes were used throughout]

No.	Cathodes				Anodes	Porous cups			
	Depth	Diameter	Capacity	Surface		Manufacture	Diameter	Depth	Treatment
	cm	cm	cc				cm	cm	
27	7	6	125	Bright...	Electrolytic...	German...	3.8	5.8	Kept in AgNO ₃
28	7	6	125	...do.....	...do.....	...do.....	3.8	5.8	
I	10	5	165	Matte...	Cast.....	American.	2.5	12.0	Kept in H ₂ O; rinsed with AgNO ₃ before use
II	10	5	165	...do.....	...do.....	...do.....	2.5	12.0	

⁴ This Bulletin, 9, p. 526.

The acidity measurements are given in Table 3.

TABLE 3

Changes in Acidity of Electrolyte for the Preliminary Experiments

[Nos. 27 and 28 are Bureau of Standards voltmeters; I and II are Princeton voltmeters]

Date	Cup	Initial acidity	Final cathode acidity	Increase, B. S. cups	Increase, Princeton cups
1914					
February 18.....	27	0.5×10^{-6}	1.2×10^{-6}	0.7×10^{-6}	
	28	0.5×10^{-6}	2.1×10^{-6}	1.6×10^{-6}	
	I	0.5×10^{-6}			
	II	0.5×10^{-6}			
February 25.....	27	0.9×10^{-6}	1.9×10^{-6}	1.0×10^{-6}	
	28	0.9×10^{-6}	2.1×10^{-6}	1.2×10^{-6}	
	I	0.9×10^{-6}			
	II	0.9×10^{-6}			
March 7.....	27	0.9×10^{-6}	2.3×10^{-6}	1.4×10^{-6}	
	28	0.9×10^{-6}	2.7×10^{-6}	1.8×10^{-6}	
	I	0.9×10^{-6}	15.7×10^{-6}		14.8×10^{-6}
	II	0.9×10^{-6}	7.3×10^{-6}		6.4×10^{-6}
March 20.....	27	0.6×10^{-6}	0.6×10^{-6}	0.0×10^{-6}	
	28	0.6×10^{-6}	1.6×10^{-6}	1.0×10^{-6}	
	I	0.6×10^{-6}	4.6×10^{-6}		4.0×10^{-6}
	II	0.6×10^{-6}	7.0×10^{-6}		6.4×10^{-6}
Average.....				1.1×10^{-6}	7.9×10^{-6}

It thus appears that the change in acidity of the electrolyte is appreciably greater in the case of the Princeton voltmeters than in the Bureau of Standards voltmeters. The reason for this appears to involve the question of the equilibrium of the porous cup and the silver nitrate solution. It will be noted in Table 2 that the method of treating the porous cups was different in the two cases. Our results showed that when the same procedure for preparing the two kinds of porous cups was employed they yielded the same results. The difference between the Princeton and the Bureau results is not, therefore, to be attributed to the fact that the porous cups were made by different makers ⁶ and from different materials.

2. FINAL COMPARISON OF THE VOLTAMETERS

Working on the assumption that the difference between the Princeton voltmeters and the Bureau voltmeters was due partly

⁶ Princeton voltmeters contained porous cups made by John Maddock & Son, of Trenton, N. J. The Bureau voltmeters contained porous cups made by the Königlische Porzellan Manufaktur, of Berlin.

to the differences in the length of time that the deposits were washed and partly to the difference in the method of preparing the porous cups, two experiments were made in which these differences were eliminated. The washings for all were done as expeditiously as possible, and the porous cups for the Princeton voltameters were put into silver nitrate solution the day before each experiment. This solution was changed several times, so that the equilibrium between the porous cup and the neutral solution might be as complete as possible and similar to the method of keeping the porous cups in silver nitrate, as has been done at the Bureau.

Table 4 gives the results of these two experiments in which some gold cathodes were also used, but we give here only the results of the platinum cathodes for comparison with Table 1. It can be seen from Table 11 that the results with the gold cathodes were equally concordant.

TABLE 4

Final Comparison of Voltameters

[Nos. 27 and 28 are Bureau of Standards voltameters; I and II are Princeton voltameters. All were dried by heating to 160°]

Date	Cup	Deposit	Mean	Difference, B. S. — Princeton
1914		mg	mg	
June 19.....	28	4113.29	4113.29	—0.5
	II	4113.31	4113.31	100 000
June 23.....	27	4133.56	4133.54	
	28	4133.53		+0.8
	I	4133.60	4133.53	100 000
	II	4133.47		
Mean.....				0
				100 000

The values obtained in these last comparisons show very perfect agreement. The changes in acidities of the electrolytes also were about the same for the two forms of voltameter. The results of the acidity measurements made as before are given in Table 5.

TABLE 5

Acidities of Final Comparison of Voltmeters

[Nos. 27 and 28 are Bureau of Standards voltmeters; I and II are Princeton voltmeters]

Date	Cup	Initial acidity	Final cathode acidity	Increase, B. S. cups	Increase, Princeton cups
1914					
June 19.....	28	0.8×10^{-6}	3.1×10^{-6}	2.3×10^{-6}	
	II	0.8×10^{-6}	2.9×10^{-6}		2.1×10^{-6}
June 23.....	27	0.8×10^{-6}	3.1×10^{-6}	2.3×10^{-6}	
	28	0.8×10^{-6}	4.1×10^{-6}	3.3×10^{-6}	
	I	0.8×10^{-6}	3.5×10^{-6}		2.7×10^{-6}
	II	0.8×10^{-6}	2.5×10^{-6}		1.7×10^{-6}
Mean.....				2.6×10^{-6}	2.2×10^{-6}

III. WASHING THE DEPOSITS

The practice of nearly all observers has been to continue the washing of the deposit until the presence of silver nitrate can no longer be detected in the wash waters by chemical tests, but many have taken the further precaution of allowing distilled water to stand on the deposit for a considerable period of time. In considering this matter we found the fact that chemical tests for the presence of silver was not particularly satisfactory when we were concerned with very small amounts of silver nitrate in the wash waters. In our final washings we were using "conductivity" water, and soon found that the change of conductivity of this water was a most admirable method for determining the completeness of the washing. The increases in conductivity, due to dissolved silver nitrate, were entirely reliable when we used a blank—that is, a clean platinum cup similarly filled with conductivity water and standing beside those containing the deposit. We could rapidly make tests of the water standing on the deposit and also that standing in the clean platinum cup. These observations showed a most unexpected state of affairs, which led to a special investigation.

It was found in the beginning that when conductivity water was put into the cups containing the deposits and allowed to stand only a short time that the increase in conductivity of the water was very small, provided of course that the silver deposits had been washed in the usual manner. This is illustrated by measurements

on the final wash water for Nos. 27 and 28 in the experiment of March 8. This last water was allowed to stand on the deposits for five minutes.

Conductivity of water originally.....	0.98×10^{-6} at 20°C
Conductivity of water taken from No. 27.....	1.00×10^{-6} at 20°C
Conductivity of water taken from No. 28.....	1.05×10^{-6} at 20°C

It was found, however, that in the case of cups I and II of the same experiment which had been washed as thoroughly as Nos. 27 and 28 that the last water which stood in them overnight showed a distinct increase in conductivity.

After standing about 10 hours we found:

Conductivity of water originally.....	1.44×10^{-6} at 20°C
Conductivity of water taken from I.....	2.85×10^{-6} at 20°C
Conductivity of water taken from II.....	3.00×10^{-6} at 20°C

This increase in conductivity suggested that some silver nitrate was actually soaking out of the crevasses, but repetitions of this soaking process showed only small differences; that is, instead of the silver nitrate all coming out on continued washing so that the water could finally stand on the deposit without sensible change, as it does in a clean platinum cup, we found that the effect would repeat itself after a number of washings.

This effect is best illustrated by the measurements made on cups I and II of the experiment of April 4. These cups had been thoroughly washed five times, and also soaked overnight, before the measurements recorded below were begun. The following table shows the increases in conductivity observed in this case:

TABLE 6

Date	Cup	Number of wash water	Duration of washing	Increase in conductivity	Increase time
1914			Hours		$\times 10^{-4}$
April 5.....	I	7	10	1.03×10^{-6}	0.103
	II	7	10	1.02×10^{-6}	.102
April 6.....	I	8	12	1.23×10^{-6}	.102 ₆
	II	8	12	1.02×10^{-6}	.085
	I	9	12	1.25×10^{-6}	.104
	II	9	12	1.06×10^{-6}	.090
April 7.....	I	10	11½	1.09×10^{-6}	.095
	II	10	11½	1.05×10^{-6}	.091
Mean I.....					.101
Mean II.....					.092

In the case of each wash water that stood on the deposit overnight we could detect the presence of silver chemically by concentrating the solution in a platinum dish to about 10 cc and testing it with potassium iodide. These tests were always conclusive and left no room for doubt that silver was actually in solution in the water.

In searching for an explanation of this phenomenon we allowed a sheet of pure silver to stand in conductivity water in a glass beaker which had been previously steamed and otherwise cleaned. The glass did not cause any significant increase in the conductivity of the water, as we had ascertained by previous experiment. When the silver was immersed in the conductivity water contained in this glass no change in conductivity was observed other than a very small, gradual increase due to contact of the air. The experiment was continued for 166 hours, and to confirm it we repeated it with another beaker and another piece of silver. The numerical results of these two experiments are given in Table 7 and plotted together as curve I in Fig. 1.

TABLE 7

[Conductivities corrected to 20° C]

Date	Sam- ple	Time	Increase in conductivity	Remarks
		Hours		
1914				
May 13.....	A	13	0.14×10^{-6}	First water.
May 15.....	B	23	0.12×10^{-6}	Do.
May 14.....	A	24	$-0.05 \times 10^{-6} (?)$	Second water.
May 16.....	B	34	0.06×10^{-6}	Do.
May 15.....	A	48	0.05×10^{-6}	Do.
May 18.....	B	70	0.04×10^{-6}	Do.
May 16.....	A	82	0.34×10^{-6}	Do.
May 18.....	A	118	0.13×10^{-6}	Do.
May 20.....	B	118	0.21×10^{-6}	Do.
Do.....	A	166	0.35×10^{-6}	Do.

Taking the final values, 0.35×10^{-6} at 166 hours for A and 0.21×10^{-6} at 118 hours for B, we find that the rate of increase for A and B are as follows: A, 0.0021×10^{-6} per hour; B, 0.0018×10^{-6} per hour. Comparing this with the results of Table 6, where the silver was deposited on the platinum, we find—I, 0.101×10^{-6} per hour; II, 0.092×10^{-6} per hour. That is, when the silver is

deposited on platinum it affects the conductivity of the water at least 50 times as fast as when the platinum is absent. Probably the effect is very much greater than this, since one may reasonably say that the increase in conductivity of the water standing on silver in the beakers is due largely, if not entirely, to dissolved substances from the glass and the contamination by the air. In any case, the observed differences are large enough to be unmistakable.

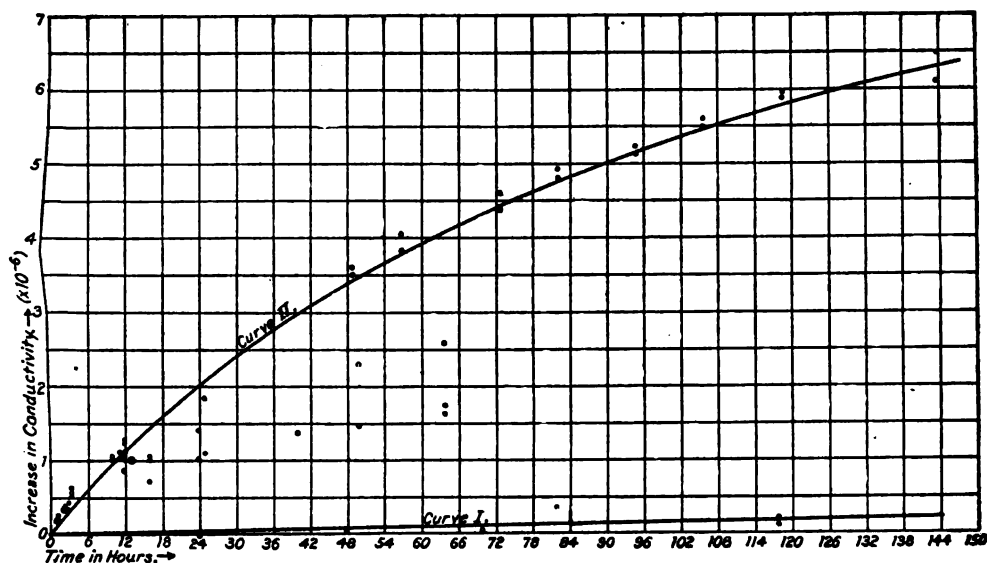


FIG. 1.—Curve I shows the negligible increase in conductivity of water standing on silver in a beaker compared with the increase in conductivity of water standing on silver deposited on platinum, as shown by Curve II

Curve II of Fig. 1 shows the increases in conductivity of the water plotted against time for all cases in which the water stood on a four gram deposit of silver in a platinum or gold cathode. (See Table 8.) The various points are results for various deposits in various experiments and made under widely varying conditions. In some cases the deposits had been dried and weighed before the deposits were put to soak in water; in other cases they were not. In some cases the results are for the third wash water and in others for even the twelfth. Consequently, it

is not surprising that the points do not lie more closely to the curve. We do not wish to lay emphasis on the position or form of the curve as we have drawn it, for this may be open to question, but the one fact that deserves attention is that all the results unite in showing that the conductivity of water standing on silver deposited in platinum increases at a much greater rate than when the water is standing on silver in a glass vessel.

We give in Table 8 complete data from which curve II in Fig. 1 is plotted. All the conductivities were measured at room temperature, which averaged about 23° and ranged from 21° to 25° . Since we were primarily interested in the increases of conductivity rather than the absolute conductivities, the corrections for temperature are negligible.

TABLE 8
Conductivities of Wash Waters

[Nos. 27 and 28 are Bureau of Standards voltameters; I and II are Princeton voltameters]

Date	Cup	No. of wash water	Duration of washing	Observed conductivity	Conductivity of water initially	Increase in conductivity	Deposit previously dried?
1914			Hours	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	
March 8.....	27	6	$\frac{1}{2}$	1.05	0.98	0.07	No.
	28	6	$\frac{1}{2}$	1.00	.98	.02	No.
March 21.....	27	6	13	2.00	1.00	1.00	No.
	28	6	13	2.00	1.00	1.00	No.
April 4.....	27	5	$\frac{1}{2}$	1.07	.93	.14	No.
	28	5	$\frac{1}{2}$	1.08	.93	.15	No.
April 5.....	27	6	12	2.01	.93	1.08	No.
	28	6	12	2.04	.93	1.11	No.
Do.....	I	7	10	2.09	1.06	1.03	No.
	II	7	10	2.08	1.06	1.02	No.
April 6.....	I	8	12			1.23	No.
	II	8	12			1.02	No.
	I	9	12			1.25	No.
	II	9	12			1.08	No.
April 7.....	I	10	11 $\frac{1}{2}$			1.09	No.
	II	10	11 $\frac{1}{2}$			1.05	No.
April 30.....	27	7	$\frac{1}{2}$	1.10	.96	.14	Yes.
	27	8	$\frac{1}{2}$	1.09	.96	.13	Yes.
	27	9	$\frac{1}{2}$	1.06	.96	.10	Yes.
May 1.....	27	9	16	2.04	.96	1.08	Yes.
May 2.....	27	10	16	1.97	.96	1.01	Yes.
	27	10	24	2.36	.96	1.40	Yes.
May 4.....	27	10	64	2.69	.96	1.73	Yes.
May 5.....	27	11	12	1.80	.95	.81	Yes.

TABLE 8—Continued

Conductivities of Wash Waters—Continued

[Nos. 27 and 28 are Bureau of Standards voltmeters; I and II are Princeton voltmeters]

Date	Cup	No. of wash water	Duration of washing	Observed conductivity	Conductivity of water initially	Increase in conductivity	Deposit previously dried?
1914			Hours	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-4}$	
May 6.....	27	12	16	1.66	.95	0.71	Yes.
	27	12	24	1.95	.95	1.00	Yes.
May 7.....	27	12	40	2.31	.95	1.36	Yes.
May 21.....	27	3	$\frac{1}{2}$	1.02	.96	.06	No.
	28	3	$\frac{1}{2}$	1.02	.96	.06	No.
	125	3	$\frac{1}{2}$	1.00	.96	.04	No.
	27	3	$1\frac{1}{2}$	1.21	.96	.25	No.
	28	3	$1\frac{1}{2}$	1.15	.96	.19	No.
	125	3	$1\frac{1}{2}$	1.15	.96	.19	No.
	27	3	$2\frac{1}{2}$	1.30	.96	.34	No.
	28	3	$2\frac{1}{2}$	1.33	.96	.37	No.
	125	3	$2\frac{1}{2}$	1.30	.96	.34	No.
	27	4	$2\frac{1}{2}$	1.32	.96	.36	No.
	28	4	$2\frac{1}{2}$	1.30	.96	.34	No.
	125	4	$2\frac{1}{2}$	1.39	.96	.43	No.
	27	4	$3\frac{1}{2}$	1.57	.96	.61	No.
	28	4	$3\frac{1}{2}$	1.48	.96	.52	No.
	125	4	$3\frac{1}{2}$	1.52	.96	.56	No.
May 22.....	I	4	25	2.77	.93	1.84	No.
	II	4	25	2.00	.93	1.07	No.
May 23.....	I	4	50	3.20	.93	2.27	No.
	II	4	50	2.40	.93	1.47	No.
May 24.....	I	4	64	3.50	.93	2.57	No.
	II	4	64	2.60	.93	1.67	No.
May 25.....	27	5	49	4.55	.96	3.59	Yes.
	125	5	49	4.45	.96	3.49	Yes.
	27	5	57	5.00	.96	4.04	Yes.
	125	5	57	4.78	.96	3.82	Yes.
May 26.....	27	5	73	5.55	.96	4.59	Yes.
	125	5	73	5.34	.96	4.38	Yes.
	27	5	$82\frac{1}{2}$	5.88	.96	4.92	Yes.
	125	5	$82\frac{1}{2}$	5.75	.96	4.79	Yes.
May 27.....	27	5	95	6.19	.96	5.23	Yes.
	125	5	95	6.09	.96	5.14	Yes.
	27	5	106	6.54	.96	5.58	Yes.
	125	5	106	6.44	.96	5.48	Yes.
May 28.....	27	5	119	6.91	.96	5.95	Yes.
	125	5	119	6.84	.96	5.88	Yes.
May 29.....	27	5	144	7.05	.96	6.09	Yes.
	125	5	144	7.44	.96	6.48	Yes.

One might readily assume that this increase in conductivity of the water is due to entrapped silver nitrate soaking gradually out,

in spite of the evidence on page 559 that the effect repeats itself indefinitely. We therefore took one of the sheets of silver used for the results recorded in Table 7 and put it to soak in conductivity water in a platinum cup. The silver rested on the bottom of the cup. The results are as follows:

TABLE 9

Date	Elapsed time	Increase in conductivity	Remarks
1914	Hours		
May 26.....	2½	None.	Water in platinum cup. No silver. Silver in the cup.
Do.....	3¼	0.06×10^{-6}	
Do.....	6¼	$.14 \times 10^{-6}$	
May 27.....	19	$.38 \times 10^{-6}$	
Do.....	30	$.58 \times 10^{-6}$	
May 28.....	43	$.86 \times 10^{-6}$	
May 29.....	68	1.40×10^{-6}	

These results are shown in the curve I of Fig. 2. For comparison we have also plotted the results when the sheets of silver stood

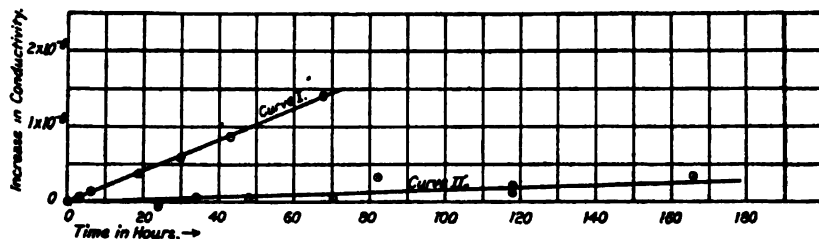


FIG. 2.—Curve I shows the increase in conductivity of water standing on a sheet of silver placed in a platinum cup contrasted with the negligible increase, shown by Curve II, when the sheet of silver and its duplicate were placed in glass beakers

similarly in a glass beaker. This is the same curve as I in Fig. 1. The difference is smaller than is shown in the curves of Fig. 1, but shows the effect quite certainly. To complete this test we boiled down the water that had stood on the sheet silver in a platinum cup and tested it chemically for silver. We found this solution to contain silver just as we had found in the case of the silver deposits referred to on page 560. In this case there was no possibility of silver nitrate producing this effect. These results indicated an electrochemical action by which the silver passed into the solution.

Accordingly, we made the following experiment to see whether evidence of an electric current passing from the platinum to the silver and into the water could be found. A platinum bowl filled with the best conductivity water was connected to the + terminal of a high-resistance potentiometer. In this and resting on the bottom was placed a sheet of silver (used in the experiments recorded above). This was connected to the negative terminal of the potentiometer. At a convenient time the silver was raised slightly and held in position in the water, but not in contact with the platinum cup. We then took the readings which are plotted

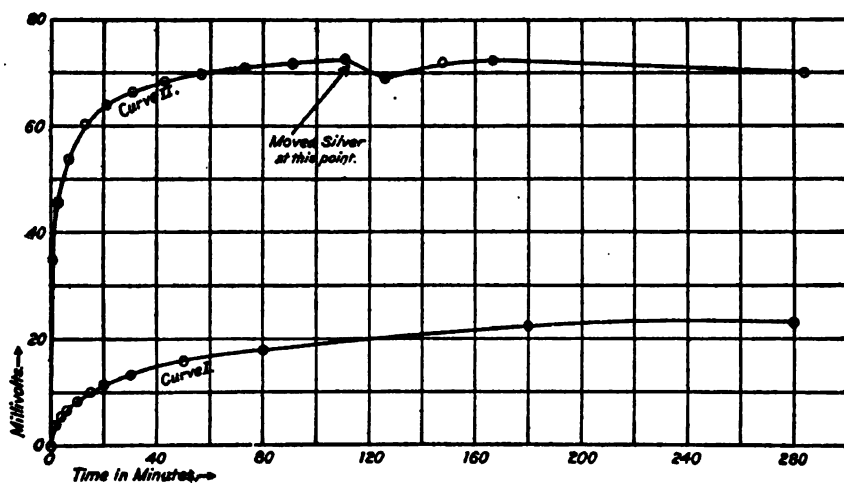


FIG. 3.—Curve I shows potential difference between a sheet of silver and the platinum cathode, the "electrolyte" being the best distilled water. The silver was raised to break contact with the platinum at time $t=0$. Curve II was obtained with a gold cathode

in the curve I of Fig. 3. Curve II shows a similar curve for a gold cup instead of the platinum. These results confirmed the idea that an electrolytic phenomenon was taking place. In a few cases we measured the loss of silver from the platinum bowl at the conclusion of the soaking process, either by estimating the silver in the water by the silver chloride produced by KCl after acidifying the solution or by reweighing the cup. We also tried estimating the silver by ammonium sulphocyanate, but without satisfactory results, because of the extremely small quantities involved. The results recorded below are not very concordant, but show that the

losses of silver from the cathode bowl are about the same order of magnitude as the amounts of silver found in the water. If we take 0.006 mg as the average amount lost to the cathode deposit per hour from 4 g of silver deposited on platinum, we see that soaking the deposit for one day of 24 hours means a loss of from 3 to 4 parts in 100 000 of a 4-g deposit, and that soaking the deposits overnight (about 16 hours) quite certainly means a loss of 2 parts in 100 000 of the deposit. In many cases the rate may be much greater than this, since probably a slightly higher conductivity in the water initially would increase the rate. Perhaps the reason that the effect seems greater at the start than after a long time is due to a gradual polarization.

TABLE 10

Date	Cup	Hours	Increase in con- ductivity	(1) Loss of silver by weighings	(2) Loss of silver by determina- tion of AgCl	Ratio: (1) Hours	Ratio: (2) Hours
1914			$\times 10^{-6}$	mg	mg		
May 1.....	27	16	1.08	0.21		0.013	
May 4.....	27	64	1.73	.34	0.49	.005	0.008
May 7.....	27	40	1.36		.20		.005
May 29.....	27	144	6.09	.67	.52	.005	.004
Do.....	125	144	6.48	.64	.53	.005	.004
Mean.....						.007	.005

Mean of all 0.006 mg per hour from 4 g of silver on platinum.

This loss of silver during the washing of the deposits, of course, shows that the deposits should be washed and dried immediately.

One further point in this connection remained to be investigated. While it seemed fairly certain from the above experiments that an electrochemical action was taking place, there still remained the possibility that a little silver nitrate entrapped behind the crystals might be slowly soaking out and adding to the observed effects. Accordingly, we tried the following experiment: Two cups, No. 27 and No. 125, of the run of May 21 were filled with water for 144 hours while an exactly similar cup, No. 28, remained dry. We scraped down half the silver deposit in No. 27 and No. 28 with a clean platinum spatula and then put 50 cc of conduc-

tivity water in each for five minutes to dissolve whatever AgNO_3 might have been trapped between the crystals and the platinum. If the soaking process appreciably lessened the amount of AgNO_3 entrapped, we should expect the conductivity of the water put in No. 28 to be increased more than that put in No. 27. The results given below show that this is not the case. To find what increase in conductivity of the water would take place, due to mere contact with the deposit not scraped down, we put 50 cc in No. 125 for five minutes also. This affords a blank experiment, and the results are to be subtracted from those found for No. 27 and No. 28. The results are as follows:

Conductivity of water initially.....	0.98×10^{-6} at 22.5°C
Blank experiment (water from No. 125).....	1.35×10^{-6} at 22.5°C
Increase to be subtracted from others.....	$.37 \times 10^{-6}$ at 22.5°C
Water from No. 27, which was soaked for 144 hours.....	1.56×10^{-6} at 22.5°C
Net increase for No. 27 after subtracting blank.....	$.21 \times 10^{-6}$ at 22.5°C
Water from No. 28, which was not soaked.....	1.49×10^{-6} at 22.5°C
Net increase for No. 28 after subtracting blank.....	$.14 \times 10^{-6}$ at 22.5°C

If we may assume that these small net increases for Nos. 27 and 28 represent silver nitrate trapped between the silver and the platinum, we may estimate the whole amount of such silver nitrate for each cup and find for No. 27, 0.03 mg; and for No. 28, 0.02 mg.

The conclusion of the whole matter is that prolonged washing of the silver deposits produces a measurable diminution in deposit, and it is therefore advisable that the deposits should be washed as speedily as possible.

IV. COMPARISON OF DEPOSITS ON GOLD AND PLATINUM CATHODES

The Princeton gold cups are quite different in appearance from those of the Bureau of Standards. The former are more yellow than the latter, which have a greenish yellow appearance. It is believed that the Princeton cups are of the purer gold. These gold cups were compared in only the last two experiments, although one of the Bureau of Standards cups was used in several previous experiments for other purposes. The results are given

in Table 10 and show the substantial agreement of the deposits on gold and platinum cathodes of both the Princeton and Bureau of Standards voltameters.

TABLE 11

Comparison of Gold and Platinum Cathodes

[Nos. 27, 28, 125, and 126 are Bureau of Standards cups; I, II, III, and IV are Princeton cups]

Date	Cup	Material	Deposit	Mean	Remarks
1914			mg		
June 19.....	28	Platinum.....	4113. 29	4113. 31	Gold-platinum = $\frac{+0.4}{100\ 000}$
	125	Gold.....	4113. 27		
	II	Platinum.....	4113. 31		
	III	Gold.....	4113. 37		
June 23.....	27	Platinum.....	4133. 56	4133. 57	Gold-platinum = $\frac{+1.4}{100\ 000}$
	28	do.....	4133. 53		
	125	Gold.....	4133. 62		
	126	do.....	4133. 58		
	I	Platinum.....	4133. 60		
	II	do.....	4133. 47		
	III	Gold.....	4133. 69		
	IV	do.....	4133. 52		

Mean excess of deposits on gold over those on platinum is $\frac{1}{100\ 000}$, which we consider excellent agreement.

These experiments do not explain the results of Dr. Buckner using the Princeton platinum and gold voltameters, where he found an excess of $\frac{12}{100\ 000}$ in the deposits on gold over those on platinum. We are at a loss to assign a reason for the differences he found, since no such differences developed in our work, but we are inclined to the belief that the cause must have been in the electrolyte. We think that the fact that such a case may arise emphasizes the necessity of making the proposed international specifications rigid in requiring platinum cathodes, since that is the most generally used.

V. COMPARISON OF POROUS CUPS FROM DIFFERENT SOURCES

The porous cups used in the Princeton voltameters were made by John Maddock & Son, of Trenton, N. J., while those used by the Bureau of Standards in its previous work, and for the most part in the present work also, were made by the Königliche Porzellan Manufaktur, of Berlin, Germany. The American-made porous cups have a great advantage in having vitreous tops, but in their original condition they are too thick to be easily prepared for the voltameter. This difficulty was overcome by grinding down the sides and bottom with carborundum paper until the walls were about 1 mm thick. Tests were made of the solubility of the porous material of both kinds of cups and these showed that after an initial washing to remove the free alkali, that the cups could stand for hours in double-distilled water without producing any significant increase in its conductivity.

In Table 11 we give a comparison of results, using these two kinds of porous cups. This table contains all the comparative results in which the porous cups were prepared, as described in the Bureau of Standards Bulletin, 9, page 185.

TABLE 12

Comparison of Voltameters Using Different Makes of Porous Cups

Date	Porous cups	B. S. vol- tammeters	<i>I</i>	Princeton vol- tammeters	<i>I</i>	Mean of all	Observer
1914		mg	mg	mg	mg	mg	
June 17.....	Trenton.....	3667.92	-0.05			3667.97	Vinal.
	Berlin.....	3668.02	+ .05				De.
June 19.....	do.....	4113.29	- .02				De.
	do.....	4113.27	- .04				De.
	Trenton.....			4113.31	0.00	4113.31	Vinal (Hulett's ap- paratus).
	do.....			4113.37	+ .06		De.
June 23.....	Berlin.....	4133.56	- .01				Vinal.
	Trenton.....	4133.53	- .04				De.
	Berlin.....	4133.62	+ .05				De.
	do.....	4133.58	+ .01				De.
	Trenton.....			4133.60	+ .03	4133.57	Hulett.
	do.....			4133.47	- .10		De.
	do.....			4133.69	+ .12		De.
	do.....			4133.52	- .05		De.

Average deviation of Berlin cups from mean, +0.007 mg; average deviation of Trenton cups from mean, -0.002 mg. The agreement of results with these two makes of porous cups is very satisfactory.

VI. SUMMARY

We have made a comparison of porous-cup voltameters that differ considerably in size and shape and particularly in the manufacture of the porous cups. We find that when the porous cups are brought into equilibrium with the electrolyte, as shown by acidity tests, all the voltameters are in excellent agreement.

We have found that when the voltameter cups containing deposits are allowed to stand filled with water (even conductivity water) a progressive solution of the silver takes place. That this is a galvanic action we have shown in several ways. The discovery of this effect makes it seem desirable to wash the deposits quickly.

Throughout the present work we have used methyl red as an indicator in the acidity measurements and have found it to be preferred to ideosine, because it is much simpler to use and at the same time gives sufficient accuracy.

PRINCETON, N. J., and WASHINGTON, D. C., July 1, 1914.

A WHEATSTONE BRIDGE FOR RESISTANCE THERMOMETRY

By C. W. Waidner, H. C. Dickinson, E. F. Mueller, and D. R. Harper 3d

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I. PRINCIPLES OF DESIGN

1. INTRODUCTION

By use of resistance thermometers, temperature measurements are frequently made to an accuracy of 0.001 and in the measurement of small temperature changes, as in calorimetry, 0.0001 or

even less is sometimes desired. The former requires resistance measurements with an accuracy of about 1 in 300 000, while the latter, involving the measurement of a small change in a large quantity, requires a precision in each measurement of the order of 1 part in 3 000 000 or more. In nearly all cases in which such measurements have been made the electrical apparatus has been of special design.

2. MERCURY LINKS AND SHUNT DIALS

To attain the above accuracy in measurements of resistances of the magnitudes usual in resistance thermometry (1 ohm to 100 ohms), the errors due to contact resistances of plugs, switches, etc., must be minimized. One familiar method of doing this is by use of mercury-cup contacts for links connecting the parts of the circuit. This is fairly satisfactory for the larger valued decades of a Wheatstone bridge, but is impracticable for several reasons in the decades comprising small fractions of an ohm. An excellent device for these which fulfills the requirement of greatly diminishing the effect of dial contact resistances is constructed on the well-known principle of changing the resistance of a circuit by shunting a small resistance with a much larger variable one.¹ The contact resistance of the switch is here a part of the shunting branch, and only a small fraction of its total variation enters into the final result.

3. IMPROVEMENTS FROM AN OLDER INSTRUMENT OF THE SAME TYPE

About 12 years ago Messrs. Waidner and Wolff, of this Bureau, designed bridges embodying the above features. The coils of the main arm of one of these bridges were of the 5, 2, 2, 1 series from 50 ohms down to 0.01 ohm, and were connected by mercury contact links. The ten steps of 0.001 ohm each were secured by shunting a fixed resistance of 0.7200 ohms with a set of resistances

¹ Such a device for producing changes in resistance by small, even-valued, and equal steps was described in a paper communicated by Waidner and Dickinson, of this Bureau, to the American Physical Society in 1904. However, the printed abstract of this communication (footnote 2) is so very condensed as to contain only a vague suggestion of the arrangement used. Since this date the device has been described by White, *Zeitschrift für Instrumentenkunde*, 27, p. 211, 1907; Diesselhorst, *Ibid*, 28, p. 2, 1908, and White, *Ibid*, 24, p. 112, 1914. Diesselhorst attributes it to White, who in turn mentions in his later paper its development several years ago by Waidner and Wolff at the Bureau of Standards.

extending from about 50 ohms to ∞ , and of values such that the change introduced in the equivalent resistance of the divided circuit was just 0.001 ohm for each step through which the controlling dial switch was turned. A similar plan with different valued coils was used for the 0.0001 ohm and 0.00001 ohm decades. This bridge is shown in Fig. 1 and has been briefly described elsewhere.² It has given very satisfactory service for over 10 years, but in the course of this time experience has suggested a number of improvements, mostly relating to convenience of operation. The more important are:

(a) Diminution or elimination of the seasonal changes of the resistance coils due to variations in atmospheric humidity. The interval between calibrations of the bridge could then be greatly extended without impairing the accuracy of work done with it.

(b) Reduction of thermoelectromotive forces occurring at the link and dial contacts when changing a setting.

(c) Simplification of the manipulation to permit of greater ease in following rapid changes of the resistances measured with the bridge.

4. GENERAL FEATURES OF A THERMOMETER BRIDGE

The following principles, dictated partly by the experience gained in the use of the older bridge, served as a basis for the design of the one here described:

(a) The coils should be hermetically sealed to protect them from the influence of atmospheric humidity.

(b) The whole bridge proper—that is, connecting switches and links as well as coils—should be immersed in the thermostat.

(c) The operating mechanism necessitated by requirement (b) should be rigidly aligned, whence all the materials of construction should be as permanent as possible. (One application of this principle was the substitution of marble for hard rubber.)

(d) The variable resistance arm should consist of six decades.

(e) The construction of the contacts and other resistance arrangements should be such that readings could be made to an accuracy of 2 or 3 per cent of one step of the last decade.

² Waidner and Dickinson: *Physical Review*, 19, p. 51, 1904. Schematic diagrams of the instrument with a few descriptive lines are given in this Bulletin, 8, p. 646, 1907; and 6, p. 153, 1909.

(f) The arrangement should be such that measurements be possible by the Siemens or the Callendar method of connecting a thermometer, or by the use of the Thomson double bridge.

(g) The arrangement should be such as to permit of calibration easily and to an accuracy indicated in paragraph (e).

II. DETAILS OF DESIGN AND CONSTRUCTION

1. GENERAL DESCRIPTION

The assembled bridge is shown in Fig. 2. The general construction is shown by Figs. 5 and 7. Upon a marble plate are mounted all the contact blocks and switches and from it also the coils are supported. All the metal parts are raised about 3 mm from the plate by small hard rubber blocks. The marble plate is mounted on four steel posts which are supported by a brass casting, the whole forming a rigid protective and supporting structure. This structure carries an auxiliary top, also of marble, to which are fastened the link lifters, handles of the dials, and other manipulating devices, but no portion of the electrical circuits. When the bridge is immersed in the thermostat oil bath the upper surface of the oil comes between the two marble plates, about a centimeter higher than the top of the contact blocks.

Diagrams showing the electrical features of the bridge are given in Figs. 11, 12, and 13, discussed in detail later. The principal parts of the bridge as built are:

(a) A pair of 100-ohm and a pair of 1000-ohm ratio coils, either pair of which can be introduced into the circuit at will and interchanged to eliminate error due to inequality of the two coils.

(b) A variable resistance arm composed of six decades, the first three being series of coils on the 5, 2, 2, 1 plan, ranging in values from 50 ohms to 0.1 ohm and connected to copper mercury-cup contact blocks provided with amalgamated copper links, and the last three being obtained by shunting resistances of 2.2 ohms, 0.34 ohms, and 0.071 ohms, respectively, with appropriate shunts (values marked on Fig. 12) to give steps of 0.01 ohm, 0.001 ohm, and 0.0001 ohm.

(c) A compensating coil of about 2.5 ohms (more exactly the value of the last three decades described in (b) when the dials are

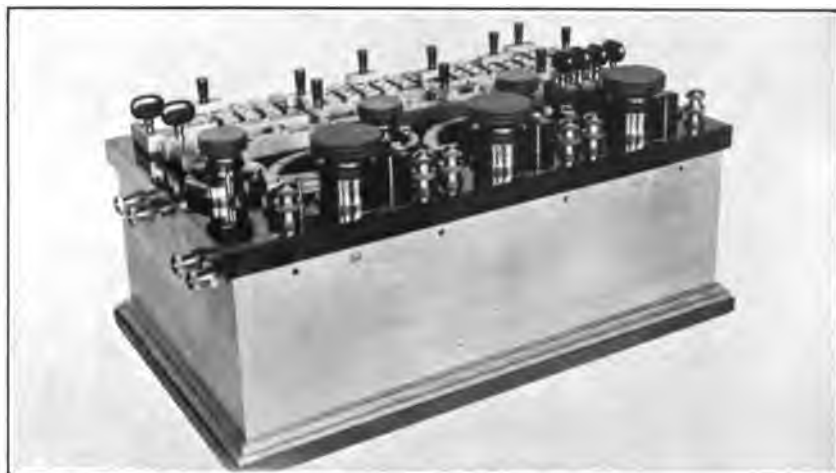


FIG. 1.—*Special Wheatstone bridge for resistance thermometry. Designed and constructed in 1903*



FIG. 2.—*Special Wheatstone bridge for resistance thermometry. Designed and constructed in 1911*

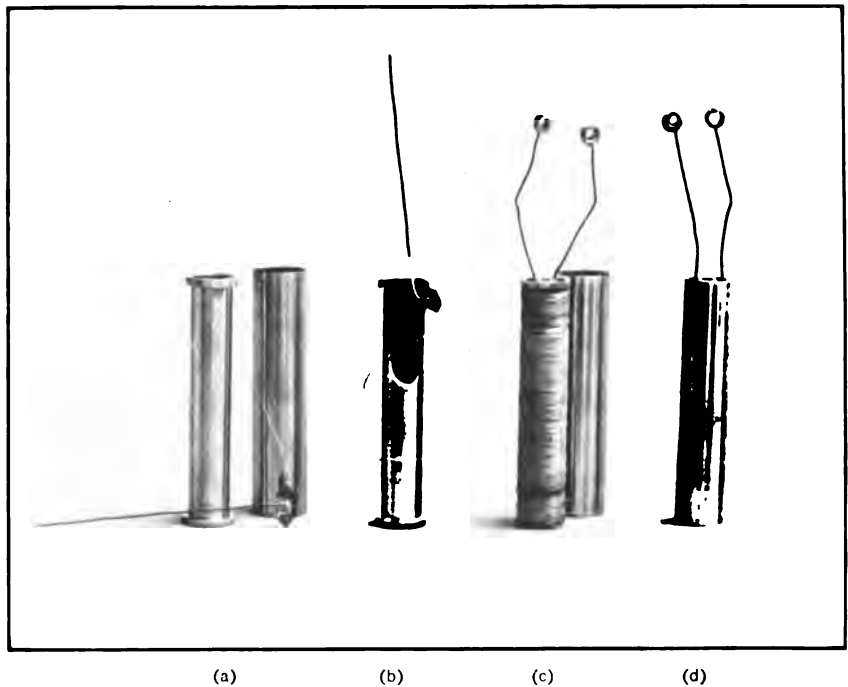


FIG. 3.—*Hermetically sealed coils for Wheatstone bridge. Details of construction*

set on zero) in the arm of the bridge in which the thermometer is to be connected, which coil makes the bridge direct reading, and permits of measuring resistances less than 2.5 ohms.

(d) Three coils and a slide wire so arranged as to provide auxiliary ratio arms which in combination with the simple bridge form a Thomson double bridge.

(e) A battery distributing switch.

(f) A galvanometer switch to change the connecting points of the galvanometer appropriately for the Thomson bridge method.

(g) Battery and galvanometer reversing switches.

(h) Sensibility switch, changing the emf applied to the bridge.

2. SEALED COILS

The investigations of Rosa, Dorsey, and Babcock³ showed the desirability of protecting resistance coils from the influence of atmospheric humidity, and developed a method⁴ of doing so for individual resistance standards, but no sealed coil suitable for use in resistance boxes has previously been developed,⁵ and the plan which has been suggested of sealing the entire box did not appear feasible. A form of sealed coil suggested by the heating coils which have been used for a number of years in the various calorimeters in the laboratories of the Bureau was developed and adopted.

The construction of the coils is shown in Fig. 3. At (a) is a group of some of the parts. The flanged metal spool will slip into the tube just to the right of it, and when the ends are soldered, there results the hermetically sealed annular space in which the wire is wound, as shown at (c). Some provision is necessary for bringing out the terminals of this wire without impairing the insulation or permitting leakage. Several devices were proposed and we are indebted to Dr. F. Wenner, of the Bureau, for the one adopted. The details are shown at (a) and (b), Fig. 3. To the point of a thin strip of sheet copper cut in the shape shown was hard soldered the

³ Rosa and Dorsey, this Bulletin, 3, p. 553, 1907; Rosa and Babcock, this Bulletin, 4, p. 121, 1907 (Scientific Paper No. 73).

⁴ Rosa, this Bulletin, 5, p. 413, 1908 (Scientific Paper No. 107).

⁵ A sealed coil is described in *Zeitschrift für Instrumentenkunde*, 33, p. 126, 1913, as a modification of a form developed by the Bureau of Standards. The reference is probably to the coil described below which was designed in 1910. (See p. 587.)

end of the insulated manganin wire of suitable size for the coil winding, and at the center of the same copper strip, perpendicular to its plane, was hard soldered a stout piece of copper wire. After providing suitable insulation, this was passed, as shown in Fig. 3 (b), through a hole drilled in the metal spool. The insulation was secured in the following way: The copper strip was covered with two layers of silk gauze, attached by painting with alcoholic solution of shellac, and the wire was wrapped beyond the bend with silk thread. When the shellac solution had dried, dry shellac was melted in, thoroughly impregnating the silk. The spool also was wrapped with shellacked silk gauze and the part to be covered by the copper strip was impregnated with melted shellac. While hot the terminal was pressed tight against the spool and permanently tied in place with silk thread. The freezing of the melted shellac formed an air-tight seal over and around the hole drilled through the spool. Melted shellac flowed into this, binding the lead wire immovably and providing excellent insulation of the latter. The use of dry shellac melted into the silk seems necessary, the use of shellac solution alone failing to give a good seal.

In Fig. 3 the terminal strip is shown bare at (a) and covered with silk at (b), the spool being bare in both cases. At (c) is shown a coil fully wound and wrapped with silk after winding. At (d) is shown a coil with cover in place, finished and ready for use.

Adjustment of the coils proceeded as follows: Very nearly the correct value was attained by using the proper length of wire in the coil winding. A closer adjustment was made, after the coil was annealed, by clipping off suitable lengths of the wire at the lower end of the coil, where the wires double back in the noninductive winding, and hard soldering these ends together. The final adjustment was made upon the leads after the coil had been mechanically completed and mounted in place. It is desirable that the external leads of the coils be of manganin, and accordingly there is considerable latitude for such adjustment. The more flexible copper is, however, advantageous at the bend, so that a copper lead should be used as described above, and then cut off just beyond the bend and a suitable size piece of manganin wire hard soldered on.

The construction described produced a coil very similar in size, shape, and general appearance to the usual form of open coil, except for the smooth brass tube instead of the furrowed outer surface and for the leads coming out from the inner spool. The carrying capacity when immersed in oil is not quite so great as for a corresponding uncovered coil, but the difference is not sufficient to be of importance. The heating for given current is about one and one-half times the heating of the open coil.

No great advantage results from the hermetical sealing of very low resistances, and in the present bridge the construction described was employed only for coils whose resistance exceeded 0.3 ohm.

3. MERCURY-CUP CONTACT BLOCKS AND LINKS

The lugs forming the terminals of the coils shown in Fig. 3 were soldered to copper posts projecting down from blocks containing mercury cups, the construction being shown in Fig. 4. When not wanted in the circuit the coil is short circuited by a link, and upon raising this the resistance of the coil is substituted for that of the copper link plus the two mercury contacts between the cups and the studs on the link. Upon the constancy of these contacts depends the reliability of the bridge and the main factor in securing the desired constancy is proper construction to secure plane surfaces and the bringing into one plane of all the four surfaces concerned. The cups were purposely made shallow, about 2 mm. deep, so as to be readily cleanable.

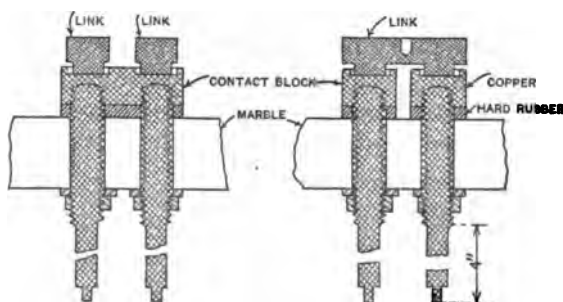


FIG. 4.—Mercury-cup contact blocks and links

The use of a rod for each coil terminal, namely, two for each contact block as shown in Fig. 4, makes the settings single valued. This is not true for a construction employing one rod for each block and attaching two coils to it at its lower end.

4. TOTAL IMMERSION IN OIL

The requirements as to accuracy make it necessary to submerge the coils of such a bridge in a thermostat oil bath, and to arrange for proper working of a convenient thermostat, the temperature at which it is set must be somewhat in excess of that of the room. If the links, etc., emerge from the oil bath into the air of the room, the temperature differences, even though small, are usually sufficient to be the cause of troublesome thermal electromotive forces. Hence, in the present bridge all parts of the electric circuits were placed within the thermostat bath. The design adopted is sufficiently well shown by Figs. 5 and 7, in connection with what has already been said under "General description," page 574.

5. LINK LIFTERS

The immersion of the links and dials in oil rendered necessary some provision for manipulating them through a cover. A second top, 6 cm above the real bridge top, was arranged as a mechanical keyboard. The links are raised from and lowered into the mercury cups by means of lifters illustrated in Fig. 6.

Although it appeared from such data as were available that mercury contacts under oil are as good as or better than the same in air, it was soon found that with link lifters which set a link down gently a very unreliable contact was obtained. The action of the oil on the mercury causes the formation of a film which must be broken before proper contact is secured. Accordingly, the lifter had to be such as to communicate to the link a motion which would break the film, and also would leave the link entirely free to rest on its own base plane when all the way down. The requirements are satisfied by the form of lifter shown in Fig. 6. A yoke fitting freely in slots in the ends of the link, together with a central pin resting in a cup in the link, permit of applying the necessary vertical pressure and at the same time "scrubbing" the contact by a small rotation of the link communicated by means of the knob forming the handle of the lifter. The extent of this rotation is limited by pins in the bushing of the lifter so that the link can never be turned far enough to fail to seat in the mercury cups of the contact blocks. When a link is lowered into place



FIG. 5.—Showing the actual bridge top with its mercury-cup contact blocks and dial switches completely immersed in oil. The cover bearing the manipulating devices is shown at the back

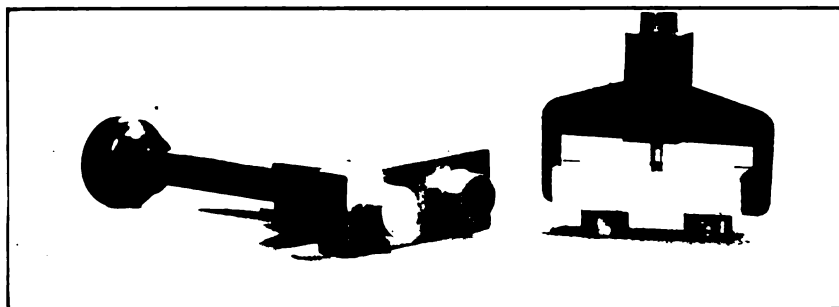


FIG. 6.—*Link and link lifter*

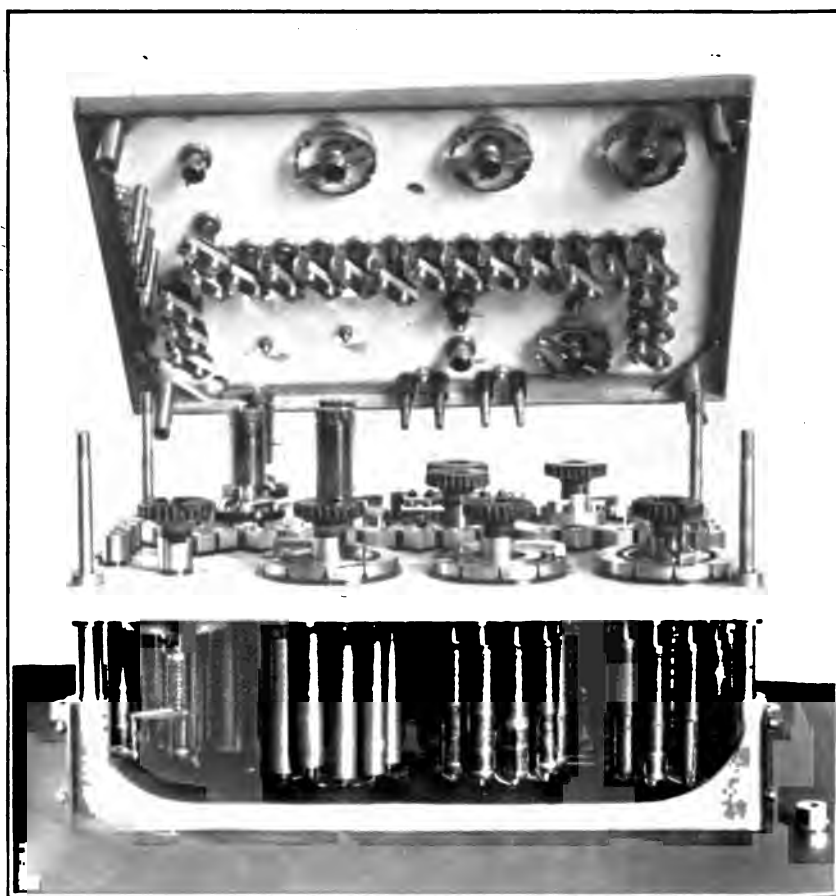


FIG. 7.—*Bridge removed from oil bath thermostat; to show rigid structural framework, mounting of coils both sealed and open, and also the details of the manipulating devices. To show the latter, the top is poised at an angle*

and the hand removed from the lifter the link is entirely free from constraint except for support by its own studs.

The operation of the dials from the top plate of the bridge is illustrated by Fig. 7. An ordinary hard-rubber dial handle with the usual clicking device was mounted on the plate, and its shaft extending downward with a cross key at the bottom engages a cross slot in the top of the dial mechanism.

6. MECHANICAL SUPPORT AND MARBLE TOP

The manipulating devices for the dials and links required careful and permanent registering with the parts below. This was secured by the use of the framework briefly described above (p. 574) and sufficiently well shown in Fig. 7 to obviate the necessity of detailed description. This frame supported the bridge in the proper position in the oil-bath thermostat.

To insure that alignment once attained would be permanent and not be destroyed by warping, marble was selected in preference to hard rubber as the material for the main plate of the bridge. The upper plate carrying the manipulating handles is also of marble. The only serious disadvantage thus incurred was a considerable increase in the mechanical difficulties of construction.

7. INSULATION RESISTANCE AND EQUIPOTENTIAL SHIELD

Since marble may be defective in insulation qualities because of veins of conducting material, the plate used was thoroughly tested for insulation. After drilling, each hole was stoppered and filled with mercury and a test made with a voltage of about 300. No insulation resistance of less than 30 000 megohms was found between any two points where metal parts were to be placed. The plate was of white marble of good clear appearance.

The presence of high potentials (relative to those in Wheatstone bridge measurements) in almost every physical laboratory makes it necessary that all electrical apparatus intended for very precise measurements shall be adequately protected from chance leakage of such stray voltage into the measuring circuit. Because of the possibility of a low surface insulation resistance, even when the best of insulating material is employed, it is desirable to screen such apparatus with a suitable metal network to equalize any differences of potential which may result in such leakage. The screen for the present apparatus was constructed by joining

electrically the copper tank containing the oil in which the bridge was immersed, metal plates in the feet carrying the board upon which the assembled apparatus was mounted, and a metal plate beneath the galvanometer.

8. LINK AND DIAL CONTACT RESISTANCES

The total resistance of a link and its two mercury contacts is about 13 microhms and is constant to about 1 microhm when operated by the form of lifter described in section 5 (p. 578) with a scrubbing motion to break up the surface film on the mercury.

The variations of resistance of the contacts of the shunt dials introduce no error greater than a microhm. By referring to Fig. 12 it will be seen that in the worst case, namely, with the largest step dial on the zero setting, the figures are as follows: 2.2 ohms is shunted by 46.2 ohms, making a joint resistance of 2.1 ohms. To change this resistance by 1 microhm the shunt of 46.2 ohms must be increased or decreased by 0.0005 ohm. With well-made dial contacts under oil this variation in contact resistance is not to be expected and has not been found.

A convenient way of stating the result deduced above, namely, that a variation of 0.0005 ohm in the shunt circuit corresponds to a change of 0.000001 ohm in the bridge circuit is to say that the effects of variation of the contact resistances are reduced 500 times. So stated, the effect is reduced 1000 and 5000 times for the zero positions of the middle and smallest dials, respectively, while on the settings at nine the figures are 50 000, 100 000, and 500 000, respectively, for the three dials, with intermediate values for the intermediate settings. It is therefore evident that even if contact resistances were liable to much greater variation than 0.0005 ohm no serious errors would be introduced.

9. RATIO REVERSING COMMUTATORS

The ratio coils are connected according to the plan shown in diagram in Fig. 11, which permits of interchanging the ratio arms of the bridge by rotating a four-point commutator through 90°. The resistance of the commutator contacts enters directly into the ratio circuit, and mercury cup contacts were constructed with the same care as for the other arms of the bridge. The details are shown in Fig. 8, which illustrates how the links are raised and

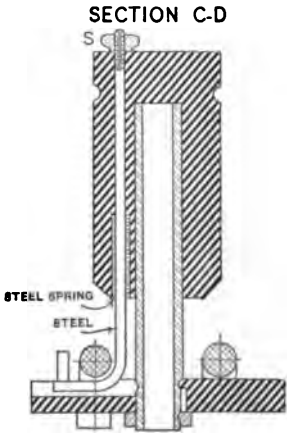
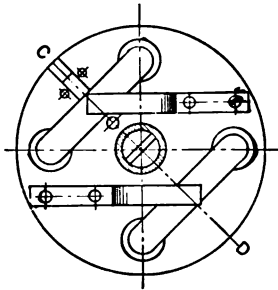
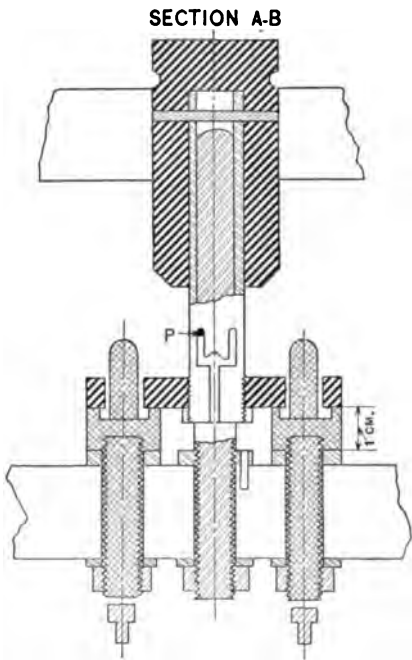


FIG. 8.—Ratio interchanging commutator



FIG. 9.—*Thermometer connectors*



FIG. 10.—*Thermometer connectors in place in mercury cup of contact block*

moved, and also are free to rest on their base plane when lowered into the cups.

In Fig. 11, for the sake of simplicity, but one pair of ratio coils is indicated. There are two pairs, one each of 100 ohm and 1000 ohm coils, connected as shown in Fig. 12. When using an equal-arm bridge connection, one of the two commutators is raised entirely clear of the mercury cups and suspended by the pin (*P*), Fig. 8. (See also Fig. 2, which shows one commutator raised and one lowered.) When using the 10:1 or 1:10 ratio, both commutator handles are lowered into position and one link of each raised by a screw (*S*), Fig. 8, so as to be out of contact with its cups.

10. THERMOMETER CONNECTORS

To secure the advantages of the mercury contacts for the bridge coils, it is desirable to have equally good contacts in connecting the thermometer to the bridge. This is done by means of connectors illustrated in Fig. 9. The flexible wires represent the thermometer leads. To these are soldered the special terminals (*a*) which fit in the mercury cups and are held securely in place by long nuts (*b*). At (*d*) is shown a similar terminal with a binding post top for making connections when a soldered connection is unnecessary or inconvenient. In Fig. 10 is shown the way in which this type of connector attaches to the bridge, the upper marble plate having been removed so as not to obstruct the view.

11. BATTERY DISTRIBUTING SWITCH AND GENERAL ARRANGEMENT OF CONNECTIONS

One terminal of the battery is connected at a fixed point in the bridge, namely, between the two ratio arms; the other terminal is left for connection at whatever point of the circuits it is desired to make the dividing point between the two remaining arms of the bridge. This depends entirely upon the use of the bridge, being different for the Siemens and Callendar pattern resistance thermometers, for measurements by means of the Thomson double bridge, for calibration, etc.

A complete diagram of connections is given in Fig. 12, and the general plan, with details omitted, is shown somewhat more clearly

by Fig. 11. The points of the battery distributing switch (Fig. 12) function as follows: The point A is connected to a binding post used for the battery connection of a Siemens type thermometer and for many general resistance measurements; B is used in conjunction with a Callendar thermometer, the main coil of which is connected in the gap 7-8 and the compensating coil at 5-6; C replaces A when both connecting leads of an external resistance are to be thrown

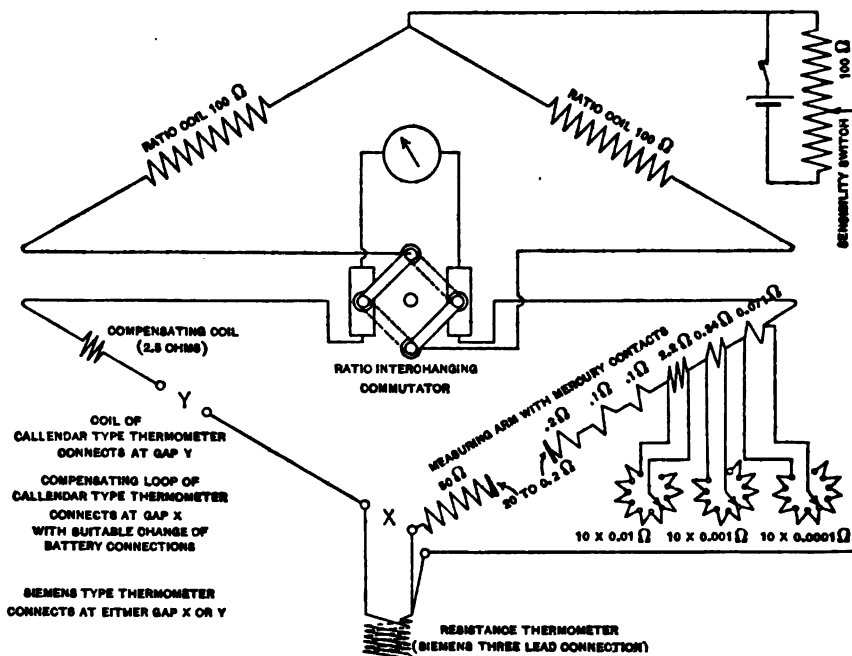


FIG. 11.—Diagrammatic representation of circuits. Connections as a simple bridge; switches for battery reversal, galvanometer reversal, etc., omitted.

into one arm of the bridge instead of so as to compensate each other; D is for checking the constancy of the mercury contact resistances⁶; E is for the Thomson bridge.

⁶ The method by which the link resistances are determined is as follows: With all the links between C and D lowered and suitable connectors in the gaps 5-8, the bridge is balanced with the battery distributor set at C and again at D. In the first instance the line of links and contacts is in the same arm of the bridge as the shunt dials; in the second instance it is in the opposite arm. Twice the resistance of this line, i. e., 36 links, is the difference in the two settings. If this be found too large, a more extended calibration is in order for the location of the faulty contact. By this arrangement—that is, having C and D permanently connected as they are—it is but a moment's work to check up the contacts, and it is therefore much more likely to be done frequently than if external connections had to be made each time.

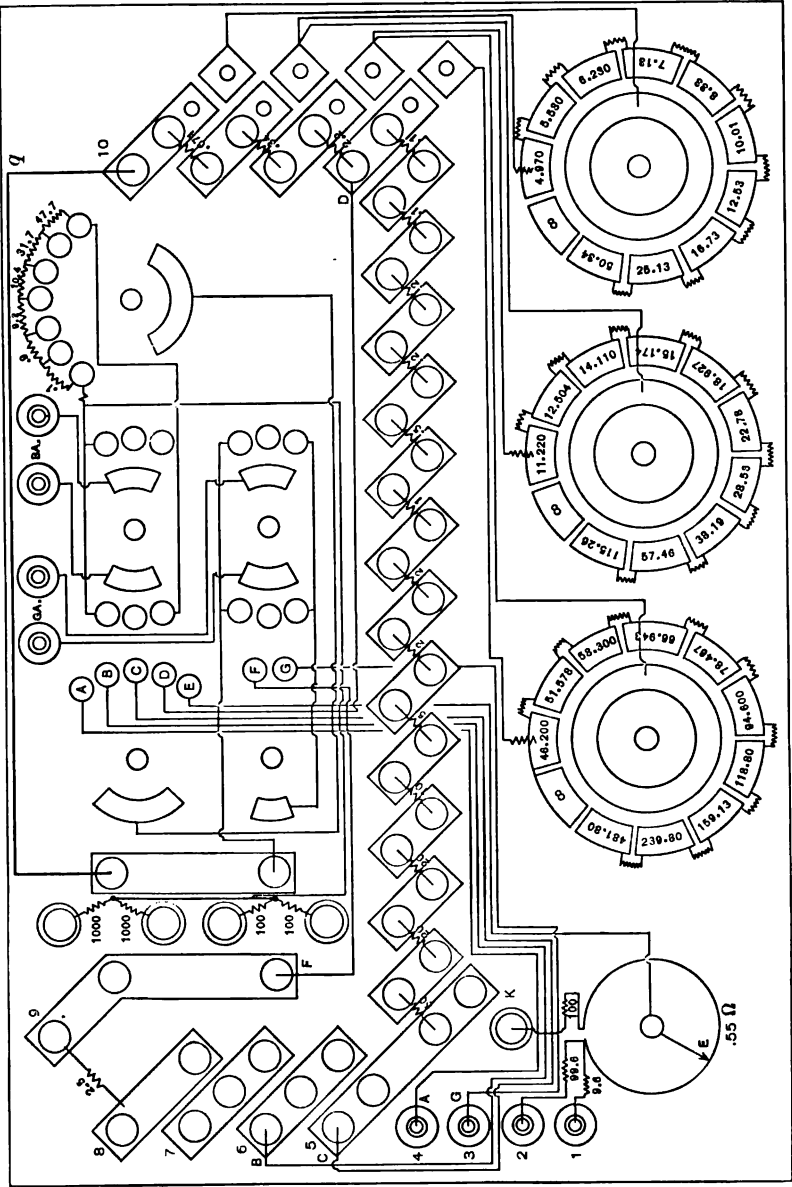


FIG. 12.—Actual connections of bridge and arrangement of bridge top

The other auxiliary switches require little explanation. The battery and galvanometer reversals are accomplished by four-point commutating switches, which include an "off" position. The sensitivity switch is in the battery line and operates by tapping off a given fraction of the applied emf. The first point corresponds to about a hundred-thousandth full sensitivity, so that a totally unbalanced bridge gives less than full-scale deflection of the galvanometer. This is very useful in determining the magnitude of an entirely unknown resistance. Successive steps increase the sensitivity until the full battery emf is applied to the bridge.

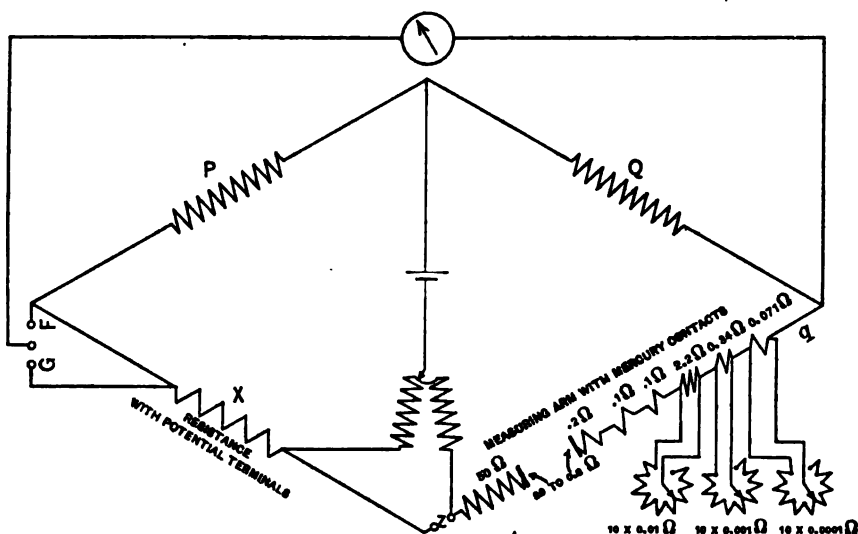


FIG. 13.—Diagrammatic representation of circuits when connected as a Thomson double bridge.

12. THOMSON BRIDGE CONNECTIONS

The diagrammatic Thomson bridge⁷ is shown in Fig. 13, and with the aid of this the actual connections may be traced out in Fig. 12, if desired. By depressing the link at K the auxiliary ratio is connected into the simple bridge at one end of the variable arm, corresponding to the arrangement shown in Fig. 13. The

⁷ The theory of the Thomson bridge can not be discussed here. The original paper on the method was published by Sir William Thomson, *Philosophical Magazine*, 24, p. 149; 1862. The subject is fully treated, with a comprehensive bibliography, in a paper by Wenner, "The Four-terminal Conductor and the Thomson Bridge," this Bulletin, 8, p. 580; 1912 (*Scientific Paper No.* 181).

gap Z (Fig. 13) is provided by the link 5-6, Fig. 12, and the auxiliary ratio and its slide wire are in the extreme lower left corner of Fig. 12. The choice of ratios, equality or 10 to 1, is clearly shown by Fig. 12 and, for the sake of simplicity, is omitted from Fig. 13.

If it be necessary to use ratio coils of high resistance, the usual method of connecting a Thomson bridge seriously limits the sensitivity attainable,⁸ so the connections shown in the figures were adopted, namely, with the resistance of the main and auxiliary ratios in the battery circuit and not directly in the galvanometer circuit, a subject which has been somewhat more fully discussed by Wenner.⁹

13. TEMPERATURE-CONTROL SYSTEM

The maximum temperature coefficient of change of resistance of any of the coils, at the temperature at which the bridge is used, is of the order of 15 parts per million per degree C, so that for resistance measurements reliable to 1 part in 3 000 000 it was necessary to provide a temperature-regulating system capable of controlling the temperature to about 0.02°. Accordingly, the bridge was immersed in a thermostat bath provided with the control system described below.

The oil is contained in a large rectangular copper tank lagged with wood, as shown in Fig. 5, circulation being forced by a motor-driven propeller in an offset tube. In the same offset tube is mounted an electric heating coil of "advance" resistance wire, a portion of the current for which is controlled so that the temperature of the bath remains constant within about 0.03° and that of the coils within 0.01°. The controlling device is a relay operated by a mercury make-and-break, the motion of which is due to expansion and contraction of the liquid in a large bulb distributed over the bottom surface of the oil bath. The relay, battery, switches, fuses, etc., are all assembled on a board at the end of the table carrying the bridge, as shown in Fig. 2.

The temperature of 30° C was selected for the operation of the bridge, and the apparatus is arranged to heat up rapidly to this temperature by using a 120-volt supply circuit, and then by the

⁸ W. Jaeger und H. von Steinwehr: *Annalen der Physik*, (4), 48, p. 1165; 1914.

⁹ Wenner, loc. cit., p. 594.

throw of a multiple-blade switch to regulate on 22 volts. A bell is connected so as to give warning when, on the rapid heating, the temperature of 30° has been reached, or if, on regulating, the relay fails to operate.

III. CALIBRATION

1. PRINCIPLES

The general principle of calibration is to compare directly the various coils and series of coils in the bridge, much as weights are compared, i. e., 50 with $20_1 + 20_2 + 10$, one such comparison being made with an external standard resistance, usually 100 ohms, so that all the results are expressible in international ohms. From these comparisons enough equations are obtained to solve for the correction to each coil.

In making such comparisons the differences between the coils are read from the small decades of the bridge, i. e., the dial shunts, and these must either be calibrated previously or else the assumption made that they are correct. The latter procedure is by far the more convenient, and if upon working down from large to small decades it should appear that the corrections to the latter were appreciable, the differences read in terms of them could then be corrected, and the calibration recomputed accordingly. No difficulty was experienced in adjusting these decades to values where the corrections are negligible, and it is not to be expected that they will change by any significant amount.

2. MANIPULATION AND APPARATUS

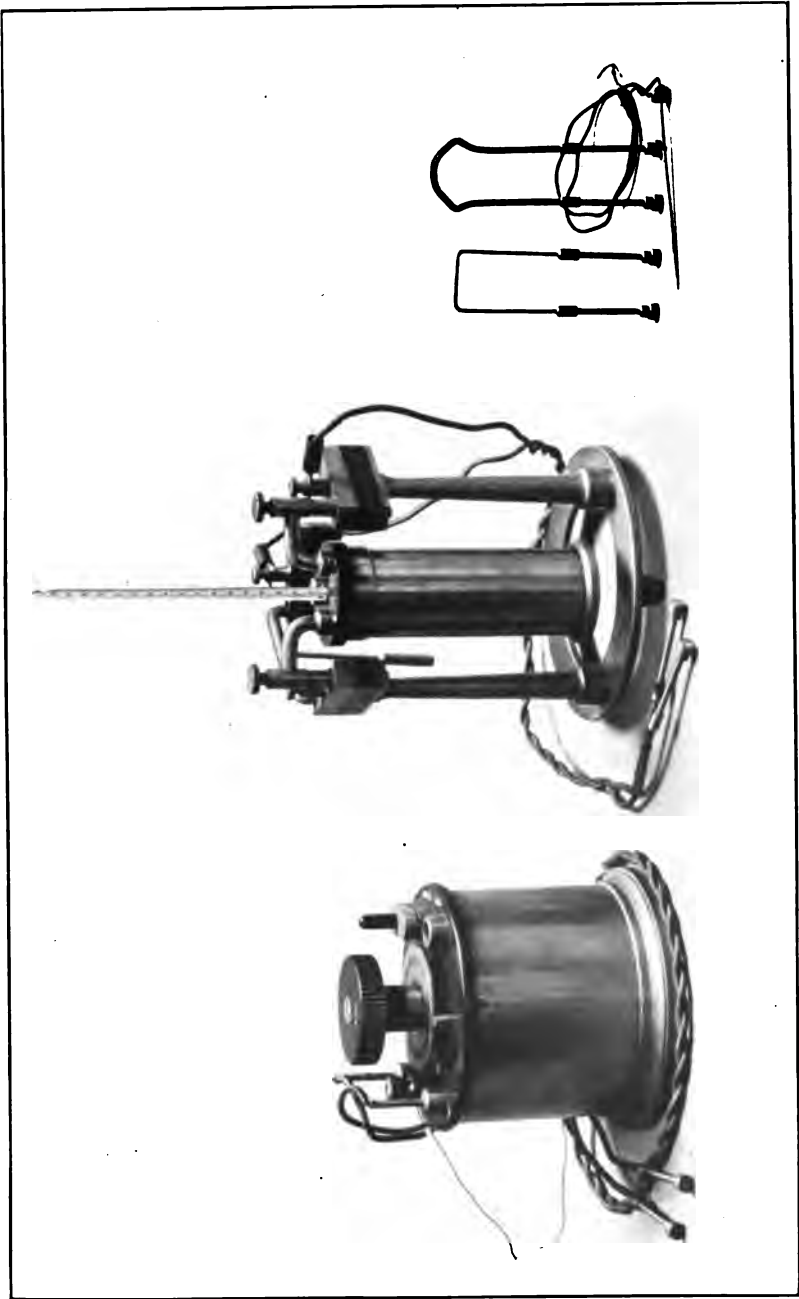
Fig. 11 will serve as the reference figure. Closing the gaps X, Y, with appropriate links, the dividing point between the two arms of the bridge, namely, the point at which the battery circuit is attached, is moved along for successive steps so as to secure the comparisons 50 vs. $\Sigma 50$, 20_1 vs. 20_2 , 20_1 vs. $\Sigma 20$, 20_2 vs. $\Sigma 20$, 10 vs. $\Sigma 10$, etc., down to 0.1, vs. 0 to 10 of the first dial. Such a comparison is made by balancing the bridge twice, once with the appropriate coils in the bridge arms and once with these short-circuited by their links. Balance of the bridge may always be obtained if a link of sufficient resistance be connected in X or Y, because the

compensating coil balances approximately the shunt-dial decades when set in their zero positions. Such a calibrating link is a small loop of copper or manganin, according to circumstances. Two of them are shown at (c), Fig. 14, together with a traveling plug used for the movable battery connection. This plug fits in a small hole at the center of each contact block (see Fig. 5), a row of small holes just over these in the cover plate being provided and stoppered with hard-rubber plugs when not so used.

The comparison of the $50 + 20_1 + 20_2 + 10$ of the bridge with a certified 100-ohm standard for the purpose of expressing all the results in international ohms is accomplished by connecting the standard in the gap X (Fig. 11) just as a thermometer would be connected. A sealed standard of the usual form is used, being shown at (b), Fig. 14, with a convenient stand, short-circuiting link, and connectors to fit the bridge.

Calibration of the dial decades is possible by at least two methods. One of these is to measure the actual values of the shunt coils and from these deduce the corrections for the bridge arm. As this method requires an auxiliary bridge adapted to the measurement of odd-valued resistances and involves rather tedious computations, another method has been deemed more convenient. This is to compare the successive steps of a dial with each other by comparing each in turn to the total interval of the next smaller dial, the steps of the last dial being intercompared by observing the galvanometer deflection produced by changing the setting one step. The method obviously requires that the dial whose total interval furnishes the comparison unit shall be set at 0 and 10, respectively, when the two balances of the bridge are secured. To accomplish this, a small variable resistance is connected in the gap X and adjusted to a value which will give the balances with the dials in the desired positions.

A variable resistance used for this purpose is shown at (a), Fig. 14. A slide wire is mounted upon a cylinder at the center of which is the bearing of an arm carrying the movable contact clip connected by a flexible lead to a binding post in the battery circuit of the bridge. The resistance of the sliding contact is therefore not in a measuring arm of the bridge. The slide wire may be shunted by suitable resistances to give it different effective values, and since



(a)

(b)

(c)

FIG. 14.—Auxiliary apparatus for calibrating bridge



the contacts for the shunts are directly in the bridge arms they are provided with mercury-cup connections.

Methods of connecting can be arranged so as to calibrate the separate parts of the shunt decades, i. e., the 2.2 ohm, 0.34 ohm, and 0.071 ohm coils, and the various connecting resistances, so that the bridge can be completely self-calibrated, a known outside resistance being needed only for the reduction from box units to international ohms.

3. SPECIAL CALIBRATION FOR THOMSON BRIDGE

For use of the apparatus as a simple Wheatstone bridge, the only calibration necessary is the determination of the substitution values of the coils in the main variable arm, the value of the steps in each dial, and the correction for inequality of ratio arms. The latter can be easily determined during the progress of any measurement. The magnitudes of the link resistances, connections, etc., are of no consequence so long as they remain constant. They are all gathered into one term and eliminated from a measurement by taking a "zero balance" of the bridge with a short circuiting link across the gap where the thermometer or other unknown resistance is connected.

For measurements with the Thomson bridge connection the same simple process can not be followed. The 2.5 compensating coil can not be used, no single step corresponding to the "zero balance" is feasible, and the absolute value of the resistance of each portion of the variable arm of the bridge must be known. Besides the series of coils 50 ohms to 0.1 ohm and their links, there are the actual values of the three shunted coils and the connecting bar, q , of Figs. 12 and 13.

IV. PERFORMANCE

The instrument was delivered to the Bureau in January 1911. The coils in it at that time were found to be imperfectly sealed, and the final set was not installed until April 1912, so that data pertaining to the behavior of the sealed coils extend over an interval of about two years. The experience with the preliminary coils during their year of service was, however, not without value.

Certain coils of the first set had failed in their insulation resistance and so were replaced by ordinary open coils; the rest were sound electrically but leaked mechanically. By the alternate heating and cooling, such a coil soon becomes filled with oil in the spaces around the winding, so that in this respect it is not to be distinguished from an open coil. However, this oil is closely confined and communicates with the larger mass of oil through very small holes only, so that diffusion of the moisture content of the oil as the seasons change is very greatly hindered, and it might be expected that seasonal variations of resistance of such a coil would be quite small. The experience with the preliminary set of some open and some "partially sealed" coils proved this to be the case. The latter were found to be very much less subject to seasonal variation than the former, and were in fact much more constant than was anticipated.

The performance of the final set of sealed coils in the measuring arm of the bridge since April 1912, is shown by Fig. 15. There is no evidence of variation related periodically to a calendar year. The standard of reference is the international ohm as given by the mean value of 10 wire standards of the Bureau, the medium for the comparisons being a 100-ohm sealed standard as already described (p. 586; also Fig. 14). Except for the 10-ohm and 5-ohm coils, the total variation of any coil with respect to the standard unit is but a trifle more than 1 part in 100 000. In view of the small magnitude of this figure, combined with the fact that the curves all show the same general peaks and depressions, the question seems pertinent as to whether the absolute variation is not as likely to be in the standard of reference as in the bridge coils.

The behavior of the mercury contacts has been satisfactory. The formation of a troublesome surface film has already been mentioned (p. 578), but after the difficulties due to this were overcome no others remained. The average resistance of a link and its two contacts is 13.6 microhms (measured as indicated on p. 582). Of this, a resistance of at least 6 microhms is in the copper, whence the order of magnitude of the resistance of each mercury contact is 4 microhms. These have been found constant within 1 microhm except when the cups were extremely dirty.

The bridge has amply fulfilled expectations with respect to flexibility and accuracy. It has proven entirely satisfactory in meeting the requirements of a general extra-precise thermometric bridge. The principal objection which users have made against it is that the rather considerable size limits portability and requires an undue proportion of the space in a complex set-up where one operator is required to be within reach of a number of instru-

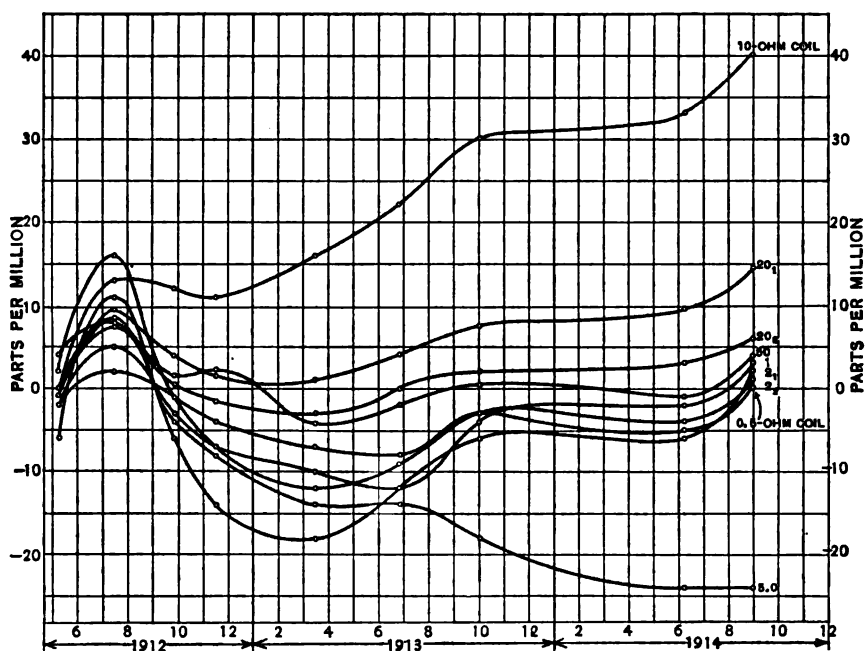


FIG. 15.—Corrections to the sealed coils (in international ohms)

ments. For a bridge of the mercury link type with the flexibility and accuracy possessed by this instrument it is not easy to see how the size can be materially reduced, but bridges of other types which are much more compact and perhaps somewhat more convenient are now being developed by the Bureau.

The Bureau is indebted to the Leeds & Northrup Co., who undertook the construction of the apparatus, for the care and skill with which many of the details of the designing as well as the construction were carried out.

V. SUMMARY

The Wheatstone bridge described in this paper was designed with especial reference to flexibility of use in measurements with resistance thermometers. The bridge is adapted to use with either the Siemens type or Callendar type of resistance thermometer, or with the potential terminal type of thermometer by the use of the Thomson double-bridge method. The instrument is also arranged so that it may be completely self-calibrated.

The 0.01, 0.001, and 0.0001 ohm decades are secured by varying, by means of dial switches, the shunts on three coils permanently connected in the measuring arm of the bridge. The sum of the resistances which are permanently connected is 2.5 ohms when the dials are set on zero, so that in order to measure resistances smaller than this a coil of 2.5 ohms is connected in the adjacent arm of the bridge.

The entire electrical circuit of the bridge, coils, contact blocks, switches, and connectors are totally immersed in an oil bath thermostat, and special manipulating devices for the links and dials, etc., are provided. Details of construction are shown by photographs and briefly explained in the text.

A new form of hermetically sealed coil, suitable for Wheatstone bridges, potentiometers, and similar apparatus, is fully described and record of its performance reviewed. Such construction eliminates the seasonal variations of resistance (with varying atmospheric humidity) found in coils of the usual types.

The accuracy attainable with the bridge is such that resistances of 1 ohm or more can be measured to an accuracy of 1 part in 300 000 in terms of the unit in which the calibration is expressed. This corresponds to an accuracy of about 0.001 for measurements with the platinum resistance thermometer. Low resistances, the accuracy of measurement of which is limited by variations in contact resistances, may be measured to about three millionths of an ohm. This figure rather than that given above for accuracy represents the precision attainable in the measurement of small changes of resistance such as are usual in resistance thermometry.

WASHINGTON, October 1, 1914.

THE EMISSIVITY OF METALS AND OXIDES

II. MEASUREMENTS WITH THE MICROPYROMETER

G. K. Burgess and R. G. Waltenberg

As indicated in a communication describing the micropyrometer,¹ this instrument may be used conveniently for the approximate determination of the monochromatic emissivities of metals, oxides, and other substances in microscopic quantities at high temperatures. This method has the further advantages of simplicity and rapidity of operation and also permits the taking of observations on rare elements, alloys, and compounds which are available only in minute quantities. It is possible, for example, under favorable conditions to measure with an accuracy of about 1 per cent the emissivity of a substance having a mass of 0.01 mg, an area of 0.25 mm², and thickness of 0.005 mm. The method lends itself readily to the determination of a temperature coefficient of emissivity and to the detection of a variation of emissivity with change of state, as at the melting point. The temperature range of the micropyrometer for these purposes is from about 700 to 3000° C.

THE METHOD

In the form here used this is a secondary method, requiring a substance of known emissivity as a comparison standard. For this purpose platinum is taken, and in what follows it is assumed that for solid platinum, at all temperatures, $\epsilon = 0.33$ for $\lambda = 0.650\mu$ and $\epsilon = 0.38$ for $\lambda = 0.547\mu$. The method is most precise for substances having an emissivity nearly equal to that of the comparison substance.

¹ G. K. Burgess, *A Micropyrometer*, Jour. Wash. Acad., 8, p. 7, 1912; Bulletin Bureau of Standards, 9, p. 475, 1912.

For the determination of its emissivity, a speck of the substance, say 0.01 mg, is placed on a platinum strip, or one of iridium or tungsten for substances melting above 1750° C, contained in a suitable atmosphere, as air, hydrogen, or in a vacuum. The strip is heated electrically until the speck melts, when, if observations on the emissivity of the solid are to be taken, the temperature of the strip is immediately lowered below the freezing point to prevent alloying. The solid substance should now have a plane, clean surface, and observations of its emissivity in terms of that of platinum may then be taken. For this purpose the micropyrometer, provided with a suitable monochromatic glass in the eyepiece, and for very high temperatures with a calibrated absorption glass before the objective of the microscope, is brought alternately to the same brightness as the platinum strip and the surface the emissivity of which is sought; the apparent temperatures of the surfaces are then measured in succession. With liquid metals observations have to be taken rapidly and before the effects of alloying have reached the surface.

The micropyrometer is first calibrated for use with a platinum or other strip by the method of known melting points (*loc. cit.*). For convenience in computation the calibration may be expressed graphically in terms of the equivalent or "black-body" temperatures p of platinum for any given wave length.² The pyrometer sighted on the platinum strip then gives p directly from which t the same true temperature of the platinum and substance is obtained graphically; sighting on the substance gives s , its equivalent temperature directly.

The emissivity, e_λ , of the substance is then calculated from Wien's equation:

$$\log_{10} e = \frac{c \log E}{\lambda} \left(\frac{1}{T} - \frac{1}{S} \right)$$

in which $c = 14\,450$, E the Napierian base, λ the wave length, T and S the absolute true and equivalent temperatures of the substance.

² See G. K. Burgess, Note on Graphic Solutions of Wien's Spectral Equation, *Jour. Wash. Acad.*, 1, p. 105, 1911.

Both tungsten and carbon lamps with fine filaments were used in the micropyrometer. Either type of lamp gave satisfactory and reliable results, the greater current sensibility of the carbon lamps about balancing the sharper photometric match of the tungsten when sighting on a metallic surface.

THE OBSERVATIONS

Measurements have been taken, mainly with red and green light of wave lengths 0.650μ and 0.547μ , respectively, of the emissivity of a number of metals and oxides over a considerable temperature range both in the solid and liquid states. The principal results for the metals are shown in Table I, together with those obtained by other observers.

It will be seen that the emissivities determined by the micropyrometric method agree for the most part with those obtained by others when working with substances upon which good surfaces may be maintained. For example, comparison of the results here obtained with those of Stubbs and Prideaux on solid and liquid gold, silver, and copper indicates differences of 0° to 5° C in the determination of the equivalent temperatures. The values found with the micropyrometer are for several other substances practically identical with those obtained by other methods; thus, compare in Table I the values for Pd, Ir, Rh, Ni, and Fe.

TABLE 1
Measurements of Emissivity of Elements

Substance	Micropyrometer observations						Other observers			
	Atmos- phere	Solid		Temp. ° C.	Liquid		At room temperatures	At high temperatures		
		Emissivity			Temp. ° C.	Emissivity				
		Temp. ° C.	λ 0.65	λ 0.55		λ 0.65			λ 0.55	Observer
Copper	H	930 1025 1080	0.096 .105 .117		1100	0.150 0.36	0.200 .11 .229 .157	Drude ³ Hagen and Rubens ⁴ Tate ⁵ Teal ⁶	0.112 .148 .16 .105 .080 .072 .077	Sold, Stubbs ⁴ Liquid, Stubbs ⁴ Burgess ⁷ Bidwell ⁹ Holborn and Henning ¹⁰ Liquid, Stubbs ⁴ Henning ¹¹
	H	940	.044	<.35	980	.072 ⁷ <.35	.047 .065 .07	Drude ³ Hagen and Rubens ⁴ Henning ¹¹	.065 .127 .130	Bidwell ⁹ Holborn and Henning ¹⁰ Solid, Stubbs and Pri- deux ¹²
	H	1000	.145	<.38	1065	.219 <.38	.105 .111	Drude ³ Hagen and Rubens ⁴	.220	Liquid, Stubbs and Pri- deux ¹²
Palladium	H	1550	.33	.38	1555	.37	.095	Teal ⁶ Wartenberg ¹² 0.35 (λ=0.579)	.125 .34 .335	Bidwell ⁹ Wartenberg ¹² Waldner and Burgess, ¹⁴ 976°
	H		.53	.38	1800	.38	.288	Drude ³	.295 1325° .335	Waldner and Burgess, ¹⁴ 1325° Waldner and Burgess, ¹⁴ 975°

TABLE 1—Continued
Measurements of Emissivity of Elements—Continued

Substance	Atmos- phere	Micropyrometer observations						Other observations		
		Solid		Liquid		At room temperatures		At high temperatures		
		Temp. °C.	Emissivity		Temp. °C.	Emissivity	Observer	λ 0.65	Observer	λ 0.65
			λ 0.65	λ 0.55		λ 0.65				
Cobalt	H	1280 to 1420	.36		1500	.37	Toll *	.319		
Iron	H	1050	.379		1535	.365	Coblentz *	.415	Bidwell, ^a 1080°	.53
		1350	.372				Drude *	.415	Bidwell, ^a 1330°	.40
		1450	.363				Hagen and Rubens *	.441	Bidwell, ^a 1430°	.38
		1530	.360				Toll *	.422	Bidwell, ^a 1530°, liquid iron	.36
							Toll *	.427	Bidwell *	.28
Manganese	H	1200	.59		1450	.59	Wartenberg, ^a 0.365 (λ=0.579)			
Titanium	H	1550	.68	.75	1800	.65				
Zirconium	H	<M. P.	.32		>M. P.	.30				
Thorium	H	<M. P.	.36	.36	>M. P.	.40				
Yttrium	H	<M. P.	.35		>M. P.	.35				
Erbium	H	<M. P.	.55		>M. P.	.30				
Beryllium	H	<M. P.	.61	.61	>M. P.	.61				
Columbium	H	<M. P.	.49	.61	>M. P.	.40	Wartenberg, ^a 0.587 (λ=0.579)	.42	Coblentz *	
Vanadium	H	1570	.35	.29	1800	.32	Wartenberg, ^a 0.425 (λ=0.579)		Coblentz *	
Chromium	H	1460	.39	.53	1550	.39	Wartenberg, ^a 0.303 (λ=0.570)	.44	Coblentz *	

Molybdenum	H	2000	.43	2500	.40	.51	Coblentz ²⁰ Coblentz ²⁰ Littleton, ²¹ 0.545 ($\lambda=0.589$)	.44 .37 .60 .45 .66 .45 .478 .69 .51	Mendenhall and Forsythe, ²² 1000°, 2400° Forsythe, ²³ 3000° Mendenhall and Forsythe, ²⁴ 1100°, 2800° Pirani, ²⁵ 1910, 3000° Pirani, ²⁶ 1912, 2000° Wartenberg, ²⁷ 1907, 3000° Wartenberg, ²⁸ 1910, 3000°
	H	1750	.39			.474			
Uranium	H	<M. P.	.55	.77	>M. P.	.34			

¹ Drude, Wied. Annalen, 39, p. 537, 1890.
² Hagen and Rubens, Annalen der Physik, 8, p. 16, 1902.
³ Tate, Physical Review (1), 34, p. 321, 1912.
⁴ Todd, Physical Review (1), 31, pp. 1-25, 1910.
⁵ Wartenberg, Verh. der Deutschen Phys. Gesellschaft, 12, pp. 105-127, 1910.
⁶ Coblentz, Bureau of Standards Scientific Paper No. 152.
⁷ Bidwell, Physical Review (2), 1, pp. 432-433, 1913.
⁸ Mendenhall and Forsythe, Astrophysical Journal, 37, pp. 380-390, 1913.
⁹ Forsythe, Astrophysical Journal, 34, p. 351, 1911.
¹⁰ Littleton, Physical Review, 30, pp. 306-311, 1912.
¹¹ Pirani, Verh. der Deutschen Phys. Gesellschaft, 12, pp. 307-348, 1910.
¹² Pirani, Physikalische Zeitschrift, 13, pp. 753-754, 1912.
¹³ Wartenberg, Berichte der Deutschen, Chemischen Gesellschaft, 40, p. 3287, 1907.
¹⁴ Foote, Physical Review, 34, p. 96, 1912.

The work with oxides (see Table 2) was done with smooth surfaces, usually with material which had been melted. This gives a surface of different character from that obtained by oxidizing a relatively heavy sheet of metal in air. We should expect the values for emissivity obtained by observing these smooth surfaces to be somewhat lower than the results of other observers using the matte surface, which is usually produced when a metal is oxidized by heating in the air. Most of the published work on emissivity of oxides has been with total radiation, but the results of Burgess and Foote²⁰ on the monochromatic emissivity ($\lambda=0.65\mu$) of nickel oxide differs slightly (2 per cent) in the direction expected, while those of Pirani¹⁷ or Rubens²⁰ on thorium oxide (0.10 and 0.08, respectively) are much lower than here obtained (0.57), a difference we are unable to explain. Our observations were taken both on the oxide placed as such on the comparison strip and that obtained by melting the metal on the strip in hydrogen and oxidizing afterwards by heating in air.

TABLE 2
Measurements of Emissivity of Oxides

Oxide of—	Micropyrometer observations					
	Atmosphere	Solid			Liquid	
		Temp. °C	Emissivity		Temp. °C	Emissivity $\lambda=0.65\mu$
			$\lambda=0.65\mu$	$\lambda=0.55\mu$		
Nickel	Air	1000 1200 1450	0.89 .83 .69	0.51 .69	1550	0.68
Cobalt	Air	1320	.77		1550	.63
Iron	Air	1200	.63		1610	.53
Manganese	Air				1600	.47
Titanium	Air	1450	.52			
Thorium	Air	1350	.57			
Yttrium	Air	1400	.61			
Beryllium	Air	1470	.37			
Columbium	Air	1450	.71			
Vanadium	Air	1160	.69			
Chromium	Air	1430	.60			
Uranium	Air	1650	.30		1700	.31

²⁰ Burgess and Foote, Bureau of Standards Scientific Paper No. 224.

²⁰ Rubens, *Annalen der Physik* (4), 20, p. 598, 1906.

In general, the oxides have higher values of monochromatic emissivity than their metallic components, although the oxides of U, Be, Mn, and Ti appear as exceptions. More difficulty was experienced in obtaining uniform results for oxides than for metals.

For the metals, most of the observations were taken in hydrogen, thus preserving a clean surface. In those cases in which it was possible to vary the atmosphere, as for palladium, platinum, and rhodium, no difference was detected in their emissivities in air, in hydrogen, and in vacuo. Most of the white metals are seen to have emissivities, both in the red and green, lying between 0.30 and 0.45.

PHENOMENA ACCOMPANYING CHANGE OF STATE

Palladium appears to have an unstable radiation behavior after solidifying in the region of its melting point. For example, the higher value 0.38 of the emissivity for $\lambda=0.65\mu$, characteristic of the liquid surface as compared with 0.33 for the solid, will occasionally persist for some time after freezing and at temperatures well below the freezing point. We are perhaps here in the presence of a radiation phenomenon analogous to surfusion, in that the molecular mechanism of the surface to which the radiation is due may maintain its liquid characteristics after freezing.

It is also of interest to note that the emissivity of platinum for $\lambda=0.65\mu$ appears to have a well-marked discontinuity at the melting point, passing abruptly from 0.33 in the solid state to 0.38 in the liquid state, an increase in red brightness of some 15 per cent on melting. This phenomenon would tend to destroy the constancy of such a standard as the Violle unit of light, which is based on the luminous radiation from the surface of platinum at its melting point.

This discontinuity of emissivity with change of state is not limited to platinum, but is very marked with red light for gold or 0.145 to 0.219, and similarly for copper and silver, while for most of the white metals, and with green light for practically all the metals examined, this discontinuity is very slight or absent; exceptions appear to be Be, Er, Cb, and U. In the case of gold

and copper, the metals may be seen to change color, from a green to an orange, on melting. With palladium mounted on platinum the abrupt change in red brightness is easily recognized, for the palladium is practically invisible until melting takes place.

TEMPERATURE COEFFICIENT

There have been published numerous observations on the temperature coefficient of monochromatic emissivity of metals, and much of this material is inconclusive or contradictory. These results are collected in Table 1, together with observations by various observers at room temperatures, based on reflection measurements, and may be compared with the micropyrometric observations of Tables 1, 3, 5, and 6.

For both white and colored metals in the solid state it will be noted that, in general, for a given wave length the value of the emissivity of a cold metal is not very appreciably different from that of the very hot metal, the difference between observed emissivities hot and cold usually being not greater than among the values obtained by several observers at high temperatures; so that the uncertainty of the existence of a temperature coefficient of monochromatic emissivity in the visible spectrum for the temperature range 20° C to the melting point is, for metals, of the same order of uncertainty as the agreement among several observers of their observations on emissivity at any given temperature, hot or cold. For example, taking the metal for which the observations are the most numerous, the average value found by nine observers of $e_{.65\mu}$ for platinum at temperatures between 970° and 1750° is 0.316, and of three observers at 20° is 0.315. The agreement, hot and cold, is for nickel about as good, or 0.358 and 0.347, respectively. For the colored metal, gold, we apparently have $e_{.65\mu}$ equals 0.116 cold and 0.127 hot in the solid state, but the emissivity is here changing very sharply with wave length, which effect may possibly account for the difference noted. In the case of iron there appears to be a slight but well-defined negative temperature coefficient of emissivity for red light, since $e_{.65\mu}$ ranges from 0.42 at 20° C to 0.38 at 1050° and 0.36 at the melting point, 1530° C, and beyond. (See Tables 1 and 3.) Nickel oxide (Table 2) shows a negative coefficient, e for red light

decreasing from 0.89 (or 0.91 according to Burgess and Foote (loc. cit.) using large sheets) at 1000° C to 0.68 at the melting point, 1452° C, and beyond.

TABLE 3
Observations on Iron
[$\lambda = 0.65 \mu$ (see p. 592 for symbols)]

Strip No.	Atmosphere	Temperature °C			State	Emissivity	
		p	s	t		Solid	Liquid
103	H	1388	1400	1538	Liquid		0.366
		1405	1426	1559	Liquid		.369
		1401	1412	1554	Liquid		.359
		1297	1317	1430	Solid	0.399	
		1212	1226	1330	Solid	.382	
		984	993	1067	Solid	.386	
141	H	1383	1397	1532	Liquid		.372
203	H	1384	1398	1534	Liquid		.367
		1383	1397	1532	Liquid		.372
205	H	1390	1405	1540	Liquid		.375
662	H	1374	1391	1521	Liquid		.382
		1337	1347	1477	Solid	.362	
		1259	1271	1385	Solid	.372	
		1197	1207	1313	Solid	.368	
		1125	1136	1229	Solid	.377	
		973	982	1055	Solid	.375	
		1060	1070	1154	Solid	.379	
		1125	1137	1229	Solid	.381	
		1193	1206	1309	Solid	.379	
		1265	1277	1393	Solid	.369	
		1337	1348	1478	Solid	.362	
		1383	1393	1533	Liquid		.354
		1331	1341	1470	Solid	.362	
		1257	1268	1383	Solid	.368	
		1187	1209	1310	Solid	.360	
		1059	1069	1153	Solid	.378	
663	H	977	986	1060	Solid	.374	
		1060	1069	1154	Solid	.375	
		1128	1140	1233	Solid	.376	
		1195	1208	1311	Solid	.380	
		1259	1271	1386	Solid	.370	
		1333	1340	1473	Solid	.350	
		1379	1390	1528	Solid	.360	
		1415	1426	1571	Liquid		.356
		1373	1385	1521	Liquid		.360
		1305	1319	1440	Solid	.372	
Mean							.368
s. d.							± .009

TABLE 3—Continued
Mean of Observations on Solid Iron

t	e
1530	0.360
1460	.362
1390	.370
1315	.374
1200	.378
1060	.378

A few observations made on alloy and carbon steels indicate a slight increase in emissivity when carbon, nickel, or manganese are present in relatively considerable quantities. (See Table 4.) The average value of $e_{.65\mu}$ for seven steels is 0.38, as compared with 0.38 to 0.36 for iron. It is hoped to make a more thorough study of the emissivity of steels.

TABLE 4
Observation on Steels
[$\lambda = 0.65\mu$ (see p. 592 for symbols)]

Strip No.	Atmosphere	Temperature °C			State	Emissivity		Analysis		
		p	s	t		Solid	Liquid	C	Ni	Mn
190	H	1385	1399	1535	Liquid		0.368	Per cent 0.08		Per cent 3.5
191	H	1377	1397	1525	Liquid		.390			
149	H	1401	1413	1554	Liquid		.362	.15		5.4
158	H	1384	1412	1534	Liquid		.380	.26		13.0
167	H	1400	1403	1552	Liquid		.391	.37		.50
211	H	1355	1368	1499	Liquid		.367	.23	15.48	.93
										Cr
398	H	1369	1383	1516	Liquid		.370	.31	2.6	1.8
									Si	Mn
702	H	1373	1384	1521	Liquid		.357	.97	.13	.12
		1305	1314	1440	Solid	0.410				
		1180	1197	1293	Solid	.396				
704	H	1283	1305	1414	Solid	.400				
		1278	1298	1408	Solid	.393				
		1151	1069	1259	Solid	.404				

PRECISION OF THE MEASUREMENTS

The precision obtainable in the measurement of monochromatic emissivities by the micropyrometric method is illustrated in Table 5 by the observations with red light on nickel in the range 1200°

to 1550° C, all of which observations are here recorded, giving for solid nickel $e_{.65\mu} = 0.356 \pm 0.008$ and for the liquid 0.367 ± 0.008 with no certain evidence of temperature coefficient and slight evidence of a discontinuity at the melting point. For a substance such as gold, possessing a very low value of emissivity in the red, and for which also observations are necessarily made at lower temperatures under less sensitive conditions, the precision obtained is shown in Table 6.

TABLE 5
Observations on Nickel
[$\lambda = 0.65 \mu$ (see p. 592 for symbols)]

Strip No.	Atmosphere	Temperature °C			State	Emissivity	
		p	s	t		Solid	Liquid
94	H	1323	1340	1461	Liquid	0.345	0.382
		1305	1309	1439	Solid		
98	H	1316	1331	1453	Liquid		.375
130	H	1316	1328	1453	Liquid		.366
218	H	1321	1335	1459	Liquid		.371
219	H	1238	1247	1361	Before melting	(*.365)	
		1315	1324	1451	Liquid		.363
		1268	1274	1396	Solid	.350	
283	H	1383	1394	1532	Liquid		.362
335	H	1320	1336	1457	Liquid		.382
438	H	1343	1352	1485	Liquid		.354
		1286	1288	1417	Solid	.358	
		1243	1249	1366	Solid	.356	
		1243	1246	1366	Solid	.344	
		1126	1134	1230	Solid	.367	
439	H	1320	1330	1457	Liquid		.362
		1330	1337	1469	Liquid		.350
		1314	1323	1450	Solid	.360	
		1304	1318	1438	Solid	.377	
442	H	1316	1325	1453	Solid	.356	
		1320	1331	1457	Liquid		.368
		1305	1315	1440	Solid	.358	
		1158	1161	1268	Solid	.340	
		1143	1150	1250	Solid	.358	
		1011	1017	1098	Solid	.361	
697	H	1314	1321	1450	Solid	.354	
		1298	1298	1419	Solid	.368	
		1140	1159	1258	Solid	.336	
Mean						.356	.367
a. d.						$\pm .008$	$\pm .008$

* Not taken for mean.

TABLE 6

Observations on Gold

[$\lambda = 0.65 \mu$ (see p. 592 for symbols)]

Strip No.	Atmosphere	Temperature °C			State	Emissivity	
		p	s	t		Solid	Liquid
104	H	1028	997	1118	Liquid		0.218
		1033	962	1134	Solid	0.136	
		1033	1006	1124	Liquid		.230
440		922	860	997	Before melting	(* .101)	
		935	886	1012	Before melting	(* .154)	
		984	926	1068	Solid	.140	
		995	961	1080	Liquid		.214
		995	940	1080	Solid	.150	
		993	938	1078	Solid	.148	
		993	965	1078	Liquid		.222
		993	938	1078	Solid	.148	
		994	963	1079	Liquid		.215
		993	941	1078	Solid	.150	
		989	926	1074	Solid	.129	
		998	965	1084	Liquid		.213
		940	872	1018	Before melting	(* .110)	
		984	932	1067	Solid	.157	
Mean						.145	.219
s. d.						$\pm .007$	$\pm .005$

* Not taken for mean.

SUMMARY AND CONCLUSIONS

The micropyrrometer has been shown to be an instrument comparable in accuracy and range with much more elaborate experimental installations for the determination of monochromatic emissivity. Starting with the cold substance, measurements of emissivity and of its temperature coefficient, accurate to about 1 per cent, may be taken at high temperatures (900 to 3000° C.) within a few minutes with a mass of less than 0.01 mg. presenting a surface of 0.25 mm².

Measurements of emissivity with red and green light have been made of 23 metals in hydrogen and 12 oxides in air; a summary of most of the results is given in Table 7.

TABLE 7
Emissivities of Metals and Oxides with Micropyrometer

Metals.....	Cu	Ag	Au	Pd	Pt	Ir	Rh	Ni	Co	Fe	Mn	Ti
$\epsilon_{\lambda=0.65\mu}$ {solid	0.10	0.04	0.14	0.33	0.33	0.30	0.29	0.36	0.36	0.37	0.59	0.63
{liquid	.15	.07	.22	.37	.38		.30	.37	.37	.37	.59	.65
$\epsilon_{\lambda=0.55\mu}$ {solid	.38	<.35	<.38	.38	.38		.29	.44				.75
{liquid	.36	<.35	<.38					.46				.75
Metals.....	Zr	Th	Y	Er	Be	Cb	V	Cr	Mo	W	U	
$\epsilon_{\lambda=0.65\mu}$ {solid	0.32	0.36	0.35	0.55	0.61	0.49	0.35	0.39	0.43	0.39	0.54	
{liquid	.30	.40	.35	.38	.61	.40	.32	.39	.40		.34	
$\epsilon_{\lambda=0.55\mu}$ {solid		.36			.61	.61	.29	.53			.77	
{liquid				.30	.81							
Oxides near F. P. s.....	NiO	Co ₃ O ₄	Fe ₃ O ₄	Mn ₂ O ₃	TiO ₂	ThO ₂	Y ₂ O ₃	BeO	CbO ₂	V ₂ O ₅	Cr ₂ O ₃	U ₃ O ₈
$\epsilon_{\lambda=0.65\mu}$ {solid	0.89	0.77	0.63		0.52	0.57	0.61	0.37	0.71	0.69	0.60	0.30
{liquid	.68	.63	.53	0.47	.51	.69						.31

In the solid state practically all the metals examined appear to have a negligible or a very small temperature coefficient of emissivity for $\lambda=0.65\mu$ and $\lambda=0.55\mu$, within the temperature range 20° C. to the melting point. Nickel oxide has a well-defined negative coefficient, at least to the melting point.

There is a discontinuity in emissivity for $\lambda=0.65\mu$ at the melting point for some but not all of the metals and oxides. This effect is most marked for gold, copper, and silver, and is appreciable for platinum and palladium.

Palladium, in addition, possesses for radiation a property analogous to surfusion, in that the value of emissivity ($\lambda=0.65\mu$) natural to the liquid state may persist for a time after solidification of the metal.

The Violle unit of light does not appear to define a constant standard.

WASHINGTON, October 24, 1914.



THE EMISSIVITY OF METALS AND OXIDES

III. THE TOTAL EMISSIVITY OF PLATINUM AND THE RELATION BETWEEN TOTAL EMISSIVITY AND RESISTIVITY

By Paul D. Foote

On the basis of the Maxwell theory, Planck¹ has derived the following equation representing the relation between the reflection coefficient of a metallic surface, the volume resistivity of the metal, and the wave length of the incident radiation:

$$(1) \quad R_{\lambda} = \frac{\sqrt{3600\lambda^2/r^2 + 1} + 1 - \sqrt{2(\sqrt{3600\lambda^2/r^2 + 1} - 1)}}{\sqrt{3600\lambda^2/r^2 + 1} + 1 + \sqrt{2(\sqrt{3600\lambda^2/r^2 + 1} - 1)}}$$

where R_{λ} is the ratio of the intensities of the reflected to the incident radiation, r the volume resistivity of the metal in ohms-cm, and λ the wave length of the radiation in cm. Defining the monochromatic emissivity as $E_{\lambda} = 1 - R_{\lambda}$ and expanding the above expression into a series of ascending powers of $\sqrt{r/\lambda}$, Hagen and Rubens² have obtained the following equation in which the terms of higher order than those indicated are usually negligible:

$$(2) \quad E_{\lambda} = 0.365\sqrt{\frac{r}{\lambda}} - 0.667\left(\frac{r}{\lambda}\right) + \dots - \dots +$$

The spectral distribution of the energy radiated by a black body may be expressed by the Planck equation:

$$(3) \quad J_{\lambda} = c_1 \lambda^{-5} \left[e^{\frac{c_2}{\lambda T}} - 1 \right]^{-1}$$

where T is the absolute temperature and $c_2 = 1.4450$ cm deg.

¹ Planck, Sitz. Königl. Ak. Wiss., Berlin, p. 278; 1903.

² Hagen and Rubens, Sitz. Königl. Ak. Wiss., Berlin, p. 466; 1910.

The total energy (any arbitrary unit) radiated by a black body is given by the integral of equation (3).

$$(4) \quad J = \int_0^{\infty} J_{\lambda} d\lambda$$

The total energy radiated by a nonblack metal may be expressed as the integral of the Planck relation multiplied by the monochromatic emissivity.

$$(5) \quad J' = \int_0^{\infty} J_{\lambda} E_{\lambda} d\lambda$$

If the total emissivity E of a metal is defined as the ratio of the energy emitted by the metal at an absolute temperature T to that emitted by a black body at the same temperature, one obtains the following relation:

$$(6) \quad E = \frac{J'}{J} = \frac{\int_0^{\infty} J_{\lambda} E_{\lambda} d\lambda}{\int_0^{\infty} J_{\lambda} d\lambda}$$

Equation (6) may be converted to the gamma function form, and is hence readily integrable. One thus obtains the following expression for the total emissivity of a metal:

$$(7) \quad E = 0.5736 \sqrt{rT} - 0.1769rT$$

where T is the absolute temperature of the radiating metal and r the volume resistivity in ohms-cm at this temperature.

It is therefore apparent that the total emissivity of most pure metals should increase with increasing temperature, both because of the increasing value of T in equation (7) and because of, in general, the increasing volume resistivity. The increase in total emissivity with increasing temperature has been observed in nearly all of the extremely few instances where this quantity has been measured.³

The above derivation is essentially that of Aschkinass,⁴ who, in an extensive paper, has discussed the energy emission of metals, the value of $\lambda_m T$ of the displacement law for metals, and the relation of various properties of the radiation from metals to similar

³ Langmuir, *Trans. Am. Elec. Chem. Soc.*, **23**, p. 321; 1913. Randolph and Overholser, *Phys. R.*, **2** (2) p. 144; 1913. Burgess and Foote, *Bureau of Standards Scientific Paper No. 224*.

⁴ Aschkinass, *Ann. d. Physik.* (4), **17**, p. 960; 1905.

properties of black body radiation. He used for the value of E_1 the first term only of equation (2), the one-term formula having been derived by Planck,⁶ but inasmuch as Hagen and Rubens⁶ have since found that the one-term relation was insufficient, it appeared of interest to derive the somewhat general relation (7) for total emissivity from the more accurate relation (2) for monochromatic emissivity. The first term of equation (7) may be obtained directly from Aschkinass's work by dividing his equation (10) by the integral of Planck's spectral equation and correcting the value of c_2 in (10) to the present accepted value of 1.445. The second term of equation (7) becomes equal to 11 per cent of the first term at 1700° C., and hence is of considerable importance, especially at the higher temperatures.

In order to check formula (7) quantitatively, measurements have been made, with Mr. Kellberg's assistance, upon the total emissivity of platinum. The apparent temperatures of thin platinum strips were measured by three radiation pyrometers of the Féry mirror type and the apparent temperatures for a wave length $\lambda = 0.65\mu$ were obtained with a Holborn-Kurlbaum optical pyrometer. The apparent temperatures measured by the optical pyrometer were converted in the usual manner to true temperatures using the value of $E_{0.65} = 0.33$. The emissivity of this metal for $\lambda = 0.65\mu$ is independent of the temperature.⁷ This is of course in contradiction to the Maxwell relation (2) above. But it must be noted that, for metals, the visible spectrum is usually the region where resonance phenomena are taking place, and hence one would here expect that the general theoretical deductions might fail to apply, as is experimentally found to be the case. This fact does not materially alter the validity of the expression (7) for the total emissivity since by far the greater part of the radiant energy of glowing metals at temperatures below 1500° C is confined to a spectral region where resonance phenomena do not exist.

The relation between the true absolute temperature T of a material, the apparent absolute temperature, S , measured by a

⁶ See note 1, p. 607.

⁶ See note 2, p. 607.

⁷ Waldner and Burgess, Bureau of Standards Scientific Paper No. 55; Mendenhall *Astrophys J.*, **28**, p. 91, 1911; Spence, *Astrophys J.*, **27**, p. 194; 1913.

total radiation pyrometer, and the total emissivity is given by the following expression:

$$(8) \quad E = \frac{S^4 - T_0^4}{T^4 - T_0^4} \text{ where } T_0 \text{ is the temperature of the receiver.}$$

The temperature coefficient of mass resistivity of pure platinum from 0 to 1100° C. is very accurately given by the Callendar⁸ parabolic equation where $\delta = 1.49$ and C the fundamental coefficient is 0.0039.

It does not appear likely that serious error is introduced by the extrapolation of this equation to the melting point of platinum. Observations by Pirani⁹, Holborn and Wien,¹⁰ and Langmuir¹¹ above 1100° C. do not deviate seriously from the parabolic relation. Langmuir concluded from his determinations that the relation was linear above 1200°, but he uses the value 1710 instead of 1755 for the melting point of platinum. If his data are corrected for the error in the temperature scale the observations follow the Callendar formula quite satisfactorily.

The mass resistivity of a 0.6 mm $\times$ 100 cm wire of Heraeus platinum, presumably of the same degree of purity as that of the strips used in the emissivity determinations, was very kindly measured by C. F. Hanson, of this Bureau, with an accuracy of about 0.1 per cent.

Reduction to the volume resistivity at 0° C. gave the value of 9.77×10^{-6} ohms-cm, with possibly an error as great as 1 per cent. The ratio r_1/r_0 determined by resistances at constant mass is equal to the ratio determined at constant volume within the accuracy of the present work.

Fig. 1 represents the total emissivity of platinum as a function of the temperature in the range 0 to 1700° C.

The computed points are represented by crosses. Preliminary observations made with radiation pyrometers which were later found to be somewhat defective are shown by small dots and the final observations made with an instrument comparatively free from these defects are plotted as circles. The large dot at 15° C.

⁸ Waidner and Burgess, Bureau of Standards Scientific Paper No. 124, p. 151.

⁹ Pirani, *Verh. D. Phys. Ges.*, 12, p. 315; 1910.

¹⁰ Holborn and Wien, *Ann. d. Physik*, 59, p. 360, 1896.

¹¹ Langmuir, *J. Am. Chem. Soc.*, 28, p. 1357; 1906.

was obtained from the work of Hagen and Rubens and others on the reflection coefficients of platinum. These investigators have determined the dispersion of the reflection coefficient to 25μ . If the values of $E_1 = 1 - R_1$ are substituted in equation (6) the total emissivity may be obtained. The integration was performed graphically. The triangles represent the observations of Lummer and Kurlbaum.¹²

The agreement between the theoretical and experimental values is excellent, when one considers the difficulties involved in an accurate determination of total emissivity. The deviations of

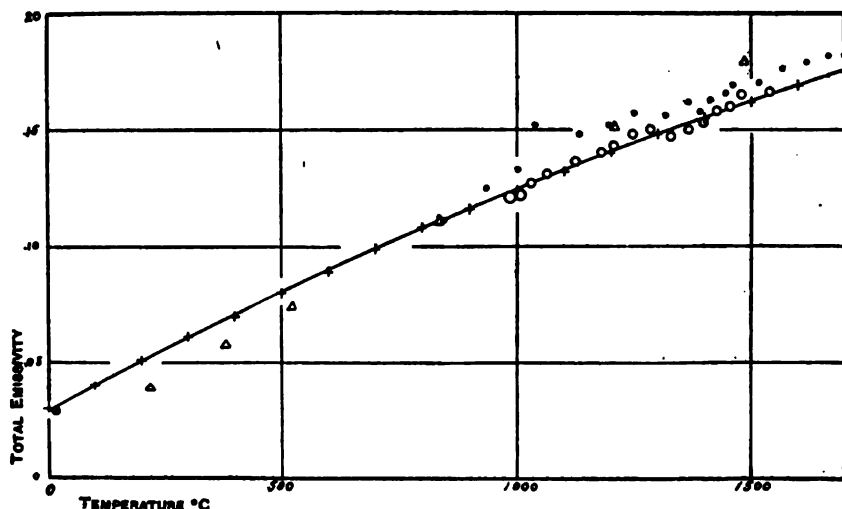


FIG. 1.—Total emissivity of platinum vs. true temperature

the computed values from the observed values are in general much less than ± 0.01 , which is about the limit of accuracy of the experimental determinations.

Table 1 presents a summary of the values of the total emissivity of pure platinum for the temperature range 0 to 1700°C .

Table 2 shows the corrections which must be applied to the temperature observed with a radiation pyrometer, when sighted upon pure platinum, in order to obtain the true temperature of the radiating platinum. The temperature of the receiver is considered as 300°abs .

¹² Lummer and Kurlbaum, *Verh. D. Phys. Ges.*, 17, p. 106; 1898.

TABLE 1
Total Emissivity vs. Temperature

Degrees centigrade	Emissivity.	Degrees centigrade.	Emissivity
0	0.030	900	0.116
100	.040	1000	.124
200	.051	1100	.132
300	.061	1200	.140
400	.070	1300	.148
500	.080	1400	.155
600	.089	1500	.162
700	.099	1600	.169
800	.108	1700	.175

TABLE 2
Total Radiation Pyrometer Sighted on Platinum
[Receiver = 300° abs.]

Observed temperature	Correction to add	True temperature
°C	°C	°C
200	365	565
300	425	725
400	475	875
500	520	1020
600	560	1160
700	595	1295
800	630	1430
900	660	1560
1000	695	1695

In a subsequent paper the emissivity of other metals will be discussed. Approximate measurements have already indicated that equation (7) is a general relation, and is by no means restricted to the example cited in the present paper. This equation, however, is somewhat modified if one considers the resistance, r , of equation (1) to be a function of λ . This modification will be discussed elsewhere.

SUMMARY

A definite relation has been found to exist between the total emissivity and the volume resistivity of a metal. This relation follows directly from the Maxwell theory of reflection and absorption. Experimental determinations of the total emissivity of platinum have verified the derived relation.

WASHINGTON, November 7, 1914.

A COMPARISON OF STELLAR RADIOMETERS AND RADIOMETRIC MEASUREMENT ON 110 STARS

By W. W. Coblentz

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1. INTRODUCTION

In a previous paper¹ thermocouples were described which appeared to be suitable for attempting to measure the radiation from stars. In addition to the sensitivity tests, made in the laboratory on artificial stars, the opportunity was presented to intercompare these instruments in connection with a large reflecting telescope.

The present paper gives the results of the laboratory tests of the sensitivity of stellar bolometers and stellar thermocouples; and also the measurements of the total radiation from various stars, made with thermocouples in connection with a large reflector.

¹ This bulletin, 11, p. 132; 1914.

The present investigation is a preliminary survey to determine what will be required in order to be able to observe spectral-energy curves of stars. We see the stars with our eyes, and it goes without saying that when we can produce instruments proportionately sensitive, it will be possible to measure the radiations from the stars.

This, of course, is not the first attempt to measure the radiation from stars. The previous attempts were the stepping stones which gave positive indications of heat from stars. However, it is but fair to say that in previous attempts experimenters were glad to be able to record definite indications of radiation from the brightest stars, let alone attempting to measure stars which were only $1/480$ as bright. The present radiometer was perhaps 10 to 150 times more sensitive than the ones used in previous work, and measurements could be made on stars as small as the six and seven-tenths magnitude. However, when one considers that stellar brightness varies by 2.512 (i. e., $\log = 0.4000$) in passing from one magnitude to the next, so that a six and seven-tenths magnitude star is only $1/479$ (i. e., $1 \div 2.51^{6.7}$) as bright as a star of zero magnitude, it is evident that a very sensitive radiometer must be used in order to detect radiation from a star which is smaller than the seventh magnitude. It may be added that with the present instruments stars of the sixth magnitude gave deflections which were as large as had been observed previously with a Nichols radiometer on stars which were more than 400 times as bright. This gain in sensitivity in one leap is of course very gratifying, but as will be noticed on a subsequent page, it is insignificant in comparison with the sensitivity that will be required in order to measure the distribution of energy in the spectra of an extensive group of stars.

Hence, while it is hoped that the present investigation will make available to the astronomer one more instrument for the investigation of celestial objects, it is desirable to emphasize, at the very beginning of this paper, that from the insensitive nature of the instrument, the astronomical application can not be very wide as compared with the spectrograph. However, its physical properties are such that, in a limited field, it can be employed in attempting the solution of some of the most fundamental questions in

astrophysics. Take, for example, the question of the emissivity of blue stars as compared with red stars. The general conclusion appears to be that blue stars are at a higher temperature than red stars, and that the emissivity of the red stars is higher than that of the blue stars. The higher emissivity of the red stars would be due to a marked change in the distribution of energy in the spectrum.

With the rather insensitive radiometric outfit used in the present investigation it was shown that the total radiation received from a red star is two to three times that of a blue star of the same photometric brightness. These observations should be extended. Another field of astroradiometric research is the measurement of the radiation from variable stars, especially those which suffer a change in color. A general radiometric survey of the stars is desirable, especially of star systems which may have companions which are too dark to detect photographically. The bright components of these stars would give an excess of total radiation as compared with other stars having the same photometric brightness. Two stars giving such an excess of total radiation were found in this preliminary survey, and no doubt many other examples will be found.

It is an easy matter to indicate problems demanding investigation. It is quite a different matter to produce the instruments for their solution. In the present paper an attempt is made to indicate the way for further improvement in the radiometric instruments. In turning now to the discussion of the results obtained in the present investigation it is desirable to emphasize once more that the advance made thus far in developing astroradiometric instruments is very small in comparison with what will be required in order to make real progress in the work.

In order to emphasize the great difference in the physical behavior of the different radiometers that may be used for measuring stellar radiation, it may be added that the thermocouple differs from the selenium and the photoelectric cells (1) in that it is nonselective to the rays of different frequencies falling upon it, i. e., it absorbs equally all the radiations of all frequencies falling upon it, and (2) in that the response to the stimulus (the heating effect) is proportional to the energy falling upon it. It is

an instrument adapted to the quantitative measurement of radiant energy. It is far less sensitive than the selenium or the photo-electric cells. The latter are not adapted for solving some of the problems discussed in the present paper.

II. BRIEF SUMMARY OF PREVIOUS INVESTIGATIONS

The measurement of stellar radiation has been attempted by three methods—(1) By means of thermoelements, (2) by means of a Nichols radiometer, and (3) by means of a selenium cell. Among the earliest attempts by means of thermoelements are the measurements of Huggins.² He used one or two pairs of elements of bismuth antimony in the focus of a refractor having an aperture 8 inches in diameter. He recorded positive deflections for Sirius, Pollux, Regulus, and Arcturus. The data given are very meager. It required from 4 to 5 minutes (15 minutes in one record) to obtain a reading.

Thermoelectric measurements of the radiation from Arcturus and Vega were made by Stone,³ who used a refractor 12.75 inches in diameter. In spite of the excessively long time (about 10 minutes) required to obtain a reading, he appears to have obtained fairly reliable results. His measurements show that Arcturus emits more radiation than does Vega, his numerical measurements for June 25, 1869, being Arcturus : Vega = 3 : 2. Considering the fact that the infra-red radiations from Arcturus suffer greater absorption than those of Vega in passing through an air mass highly saturated with water vapor, and in passing through the glass lenses of the refractor this ratio (3 : 2) is in close agreement with subsequent measurements using a reflecting telescope.

Recent measurements of stellar radiation were made by Pfund,⁴ using thermocouples in an evacuated receptacle. The receivers attached to the junctions of the bismuth alloys (BiSn—BiSb) were about 1.2 mm in diameter. The sensitivity was such that the radiation from a Hefner lamp at a distance of 1 m gave a deflection of 2400 mm. He used a reflecting telescope 30 inches in diameter, and made measurements on Vega (7.5 mm "double deflection"), Jupiter (part of disk, 3 mm), and Altair (2.0 mm

² Huggins, *Proc. Roy. Soc.*, 17, p. 309; 1868-69.

⁴ Pfund, *Publ. Allegheny Obs.*, 2, p. 43; 1913.

³ Stone, *Proc. Roy. Soc.*, 18, 159; 1869-70.

deflection, sky hazy). The ratio of the radiations Vega + Altair = 3.7, which is at variance with the results obtained in the present investigation, and emphasizes the importance of making observations through an atmosphere free from water vapor. He concluded that with a more sensitive galvanometer, and one of the largest reflectors it would be possible to observe stars to the fourth magnitude.

An extensive series of measurements of the radiation from Arcturus, Vega, Jupiter, and Saturn were made by Nichols⁶ by means of his radiometer which, like the thermopile, absorbs all the radiations of all wave lengths falling upon it. The receivers were 2 mm in diameter. A candle at a distance of 1 m would have given a deflection of 724 mm. He used a 2-foot reflector and observed deflections of 1 to 2 mm. In fact, deflections which were larger than 2 mm were considered false, while frequently they were of wrong sign. The sensitivity of his radiometer was such that a deflection of 1 mm would be caused by 1/68 750 000 of the heat received on a surface equal to the aperture of the concave mirror from a candle at 1 meter distance. Or, neglecting atmospheric absorption, the sensitivity was such that by using the 2-foot mirror to focus an image of the flame upon the radiometer he would have obtained a deflection of 1 mm from the candle placed at a distance of 5 miles. He concluded that the thermal intensity was Vega: Arcturus: Jupiter: Saturn = 1 : 2.2 : 4.7 : 0.74. As for the possibility of further work he concluded that by using a 5-foot reflector it would be possible to observe white stars down to the second magnitude and red stars possibly to the third magnitude.

The Boys⁶ radiomicrometer has also been tried in measuring radiation from stars. The instrument was used with a 16-inch reflecting telescope. The slight deflections obtained on various planets and stars were regarded as of questionable origin.

The earliest measurements of the light from stars by means of a selenium cell were made by Minchin,⁷ who used a 2-foot reflector. He examined about a dozen stars, some being as small as the third magnitude. Owing to the peculiar properties of the selenium cell, which is highly selective in its response to radiations of different

⁶ Nichols, *Astrophys. J.*, 18, p. 101; 1901. ⁷ Minchin *Proc. Roy. Soc.*, 58, p. 142, 1895; 59, p. 231, 1896.

⁶ Boys, *Proc. Roy. Soc.*, 47, p. 480; 1890.

wave lengths, the data can not be used in comparing the radiation from different stars. The selenium cell can be applied, however, in the measurement of the maximum and minimum of light emission from a variable star which does not change in color. For this purpose it has been used by Stebbins⁸ in connection with a 12-inch refractor.

III. APPARATUS AND METHODS USED IN THE PRESENT INVESTIGATION

Under this title are given only the main outlines of the instruments used in this research. For a more complete description it is necessary to consult the original papers to which frequent reference is made.

1. THE GALVANOMETER

The electric current generated by the thermoelements was measured by means of an ironclad galvanometer,⁹ consisting of four coils of wire embedded in blocks of Swedish iron, as shown in Fig. 8 of this bulletin, 11, page 180, 1914. The coils were wound in three sections of Nos. 38, 34, and 28 B. S. gauge (lengths of wires 3, 8, and 32 meters). They were 33 mm in diameter and had a resistance of about 20 ohms, or 5.3 ohms when all four coils were joined in parallel. The suspended system consisted of two groups of magnets, four in each group. They were about 1.6 mm long, 0.25 mm wide, and 0.08 mm thick, made of fine tungsten steel. The mirror was 2 by 2.5 mm. The complete system weighed about 6 mg, which is rather heavy. The deflections were read by means of a telescope and scale placed at a distance of 2 m from the galvanometer mirror. The magnetic shields consisted of an inner shield of about 15 turns of transformer iron 0.6 mm in thickness. There were three additional shields of soft iron pipe which were, respectively, 12, 16, and 18 cm in diameter.

The galvanometer stood upon the south pier which forms one of the two supports of the polar axis of the reflecting telescope. The galvanometer was therefore very close to the heavy iron telescope tube. In spite of this fact the rotation of the telescope tube affected the galvanometer only when the reflector was directed

⁸ Stebbins, *Astrophys. Jour.*, **32**, 185, 1910; **33**, 385, 1911.

⁹ This Bulletin, **9**, p. 61, (1911) 1913; **11**, p. 131, 1914.

upon stars situated low on the northern horizon, which brought the lower end of the telescope tube within 1 m of the galvanometer.

Most of the operations about the reflector are performed by electric motors. It was found that the winding of the driving clock, which occurred every 20 minutes, did not interfere with the observations. The rotation of the telescope is accomplished by means of two sectors. The electric motor which disengages one sector and engages the second was found to slightly affect the galvanometer. However, this changing of sectors occurred but once per hour and did not interfere with the work. Rotating the dome and changing the height of the movable observing platform (both operations being performed by heavy motors which moved with the dome) usually affected the astaticism and hence the sensitivity of the galvanometer, especially when the dome was open to the south, which brought the movable parts close to the galvanometer. After each setting on a new star, it was therefore usually necessary to adjust the galvanometer reading upon the scale. This could be accomplished in a few moments, so that it was possible to observe three to four stars per hour. The galvanometer sensitivity ($i = 1.4 \times 10^{-10}$ ampere for a single swing of about four seconds) used in this work was not any higher than that ordinarily used in the Bureau of Standards. The galvanometer deflection attained a maximum in three to four seconds, so that it was possible to obtain a reading in six to seven seconds. In fact most of the observations were obtained in about five seconds.

The observations on stars which were made on the first two or three nights were for the purpose of comparing the sensitivity of the various thermoelements, and for determining whether a special pier would have to be constructed for the galvanometer. When it was found that the galvanometer could be used when situated upon the telescope pier, and that a high sensitivity would not be required in making a preliminary radiometric survey of celestial objects, the work was promptly begun. In future work, a special pier, situated at some distance from the telescope, will be necessary in order that the galvanometer may be used on a higher sensitivity.

In a previous paper¹⁰ attention was called to difficulties which may arise when small particles of iron become attached to the magnet system. A similar difficulty was experienced in the beginning of the present investigation. The galvanometer deflection could not be kept in the field for any length of time, and after each deflection the mirror would take a new zero reading. When examined under a microscope a minute particle of magnetic material was found adhering to one of the small magnets. After removing this material no further difficulty was experienced with the astaticism.

In regard to the wiring equipment it may be added that the lead wire from the galvanometer to the thermocouples was a heavy cable of flexible wires (No. 16) which had an extra covering for

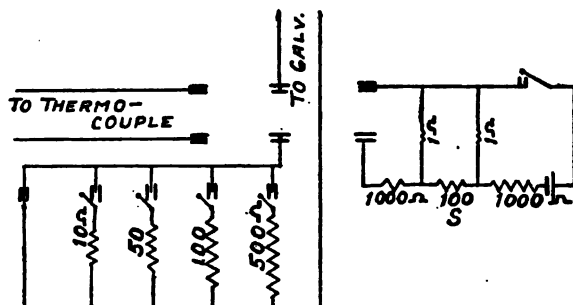


FIG. 1.—Electrical connections

insulation. The total length of this "twisted lamp cord" was 10.1 m, the resistance being 0.3 ohm. A special switchboard was provided with a double-pole, double-throw switch which enabled the observer to connect the galvanometer to a special sensitivity testing device, *S*, Fig. 1, and in this manner determine the current sensitivity of the galvanometer. This was done at the beginning and end of a set of measurements on a star. The electrical connections, consisting of resistances for reducing the sensitivity of the galvanometer (which was necessary in measuring the radiation from Venus) and the sensitivity testing device, *S*, are shown in Fig. 1.

In conclusion, it is desirable to emphasize that a very much higher galvanometer sensitivity could have been used if time had

¹⁰ This Bulletin, 9, p. 61; 1911.

been taken to construct a special pier for the instrument, situated at some distance from the telescope. A higher galvanometer sensitivity could have been attained by using a lighter suspension and by placing the instrument in a vacuum.

2. THE VACUUM THERMOCOUPLES.

At various times during the past three years stellar thermopiles were constructed. In the early attempts several (one instrument had 10 thermojunctions¹¹) were placed in a small space with a receiver 1 mm in diameter, covering the junctions. However, in view of the fact that a star image is a mere point of light anyway, the mode of construction was entirely reversed. The utmost simplicity of construction was undertaken. Instead of several thermojunctions (a thermopile), single thermocouples were constructed. The materials used are of the smallest workable dimensions in order to reduce the heat capacity. In fact, the high radiation sensitivity attained was found¹² to depend more upon low heat capacity and low heat conductivity than upon a high thermoelectric power of the material used.

The receivers attached to the thermoelements were 0.3 to 0.4 mm in diameter. From two to three of these elements, as shown in Fig. 2, were mounted in an exhausted glass receptacle, and the best one was used in the stellar radiation measurements.

The general construction of the instrument is shown in Fig. 2. Platinum (No. 26) lead wires are sealed into a glass tube, *T*, which in turn is sealed into a thick disk of plate glass, *G*, by means of Khotinsky ("hard") cement, *K*. The glass disk, *G*, which forms the rear window of the thermoelement container, Fig. 3, is attached by means of stopcock grease covered with Chatterton wax, which is sufficiently elastic to prevent cracking and leaking.

The method of construction of these delicate thermocouples is given elsewhere¹³ and it will be sufficient to add a few details with reference to the elements used in the present work. The mounting known as No. 7, shown in Fig. 2, contained two thermocouples. The upper one, No. 1, consisted of bismuth (length

¹¹ This Bulletin, 9, p. 30; 1911.

¹² This Bulletin, 11, p. 1317; 1914.

¹³ This Bulletin, 11, p. 1317; 1914.

2.2 mm, width 0.067 mm) and an alloy¹⁴ of bismuth + 5 per cent tin. The elements of alloy were short pieces, perhaps 1.5 mm in length, which were attached to the heavy platinum lead wires by means of fine silver wire. The receivers were, respectively, 0.383 (No. 7 (1a)) and 0.441 mm in diameter. They were made by pressing small globules of tin between pieces of plate glass.

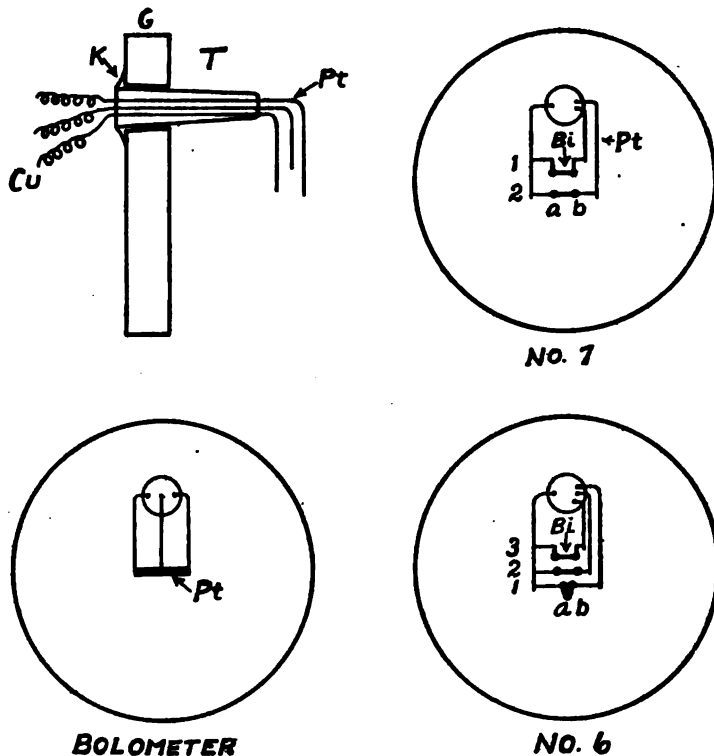


FIG. 2.—Stellar thermocouples

The resistance of No. 7 (1) was 111.8 ohms. A similar element of bismuth and of bismuth tin alloy, 3, was used in mounting

¹⁴ The method for producing fine wires and thin plates mentioned in this Bulletin, 11, p. 150, 1914, was first discussed in Bulletin 7, p. 248, 1910. In the latter no mention is made of the fine wires which are produced by spattering the molten metal by dropping it from a height upon a glass plate, for at that time wide strips were desired for radiomicrometer vanes. Both fine wires and thin plates are unavoidably produced by this "method," which at that time seemed of too little importance to merit description. In a letter dated Nov. 16, 1914, Dr. Pfund challenges the priority of this "method" as compared with his, which consists in hurling the molten material across a glass plate. No priority is claimed nor desired. This note is added in response to the request of the aggrieved party that the matter be set aright in print.

No. 6, shown in Fig. 2. The receivers were, respectively, 0.335 mm (No. 6 (3b)) and 0.345 mm in diameter. They were made by pressing flat between thin plates of mica a molten globule of Wood's alloy which was used as a solder. The receivers were not quite round, which made it difficult to estimate their area. The resistance of this thermocouple was 12.2 ohms.

The mounting, No. 7, contained also a thermoelement, 2, of bismuth-platinum. The length of the bismuth was 1.9 mm and the width was 0.071 mm. The receivers, made of flattened globules of tin, were, respectively, 0.29 and 0.33 mm in diameter. The platinum wires were about 0.01 mm in diameter and perhaps 1.5 mm in length. The resistance was 4.58 ohms.

Similar thermoelements of bismuth-platinum were in container No. 6. Unfortunately the best one, 2, was broken in carrying the instruments up the mountain road. The thermocouple, 1, consisted of a thin strip of bismuth (length 2 mm; width 0.05 mm) which was folded in such a manner that the two receivers were close, side by side. The platinum wires were longer than in No. 7 (2), which probably accounts for the high resistance, 9.0 ohms, of this element. The receivers were thin disks of tin, 0.45 mm in diameter. The object in placing the two receivers close together was to enable the operator to quickly expose the receivers alternately to a star image and thus double the galvanometer deflection. In practice, however, only one receiver was exposed to the radiation from a star.

All the receivers were painted with a mixture of lampblack and platinum black, as previously described. The difficulty experienced was that the paint would not always adhere uniformly close to the edge of the receivers, so that in repainting the edge the thickness of the absorbing layer is not always uniform over the whole surface of the receiver. This may account for the difference in sensitivity of some of the receivers. As recorded in a previous paper,¹⁵ the reflecting power of the lampblack paint is higher than that of soot deposited from a candle. After applying the paint to these receivers they were touched with a piece of blotting paper wet with alcohol, which after evaporation seemed to produce a surface as black and as

¹⁵ This Bulletin, 9, p. 283; 1913

fine grained in structure as is a surface of electrolytically deposited platinum black.

The main portion of the receptacle inclosing the thermocouples consists of a single piece of glass, *E*, Fig. 3, with a projecting glass tube which contains potential terminals, *P*, for testing the evacuation. A fluorite window, *F*, admitted the stellar radiations into this glass vessel, and upon the thermocouples which are supported by the platinum wires to be seen through the glass container, *E*. The fluorite window was attached with stopcock grease and around the edge was placed Chatterton's compound.

This peculiar form of construction was necessary in order to be able to use the device when attached to the plate holder, in the focus of the telescope mirror. The star image and the receivers of the thermocouple are viewed from the side of the large telescope tube by means of a right-angled prism and a lens, which are mounted close to the glass window, *G*, Fig. 3, and which are part of the the permanent plate-holder equipment of the telescope. It was therefore necessary to design the radiometric attachment so that all the projecting parts extended downward in the direction of the reflecting mirror.

The attachment, *L*, containing the reflecting prism and the lens is shown in Fig. 4. The glass receptacle containing thermoelements is mounted in a metal box, *B*, which is attachable to the permanent equipment, *L*, by means of screws, *S*, *S*. In this manner it was possible to quickly replace the radiometric attachment by the regular photographic plate holder. The box, *B*, could be rotated about the optic axis of the telescope. An absorption cell of water, 1 cm in thickness, is contained in the hinged metal box, *A*. The attachment, *B*, was made in Washington and fitted to the telescope, *L*, after arrival on Mount Hamilton.

It may be added that the resistance of the fine platinum wire used is very high (2 to 3 ohms per millimeter), but a length of only about 1.5 mm. of platinum wire is required. The platinum wire is attached to a piece of silver wire 0.0165 mm. in diameter, which in turn is attached to the heavy lead wires. A globule of tin is attached to the platinum wire and pressed flat to form the receiver as described in a previous paper.

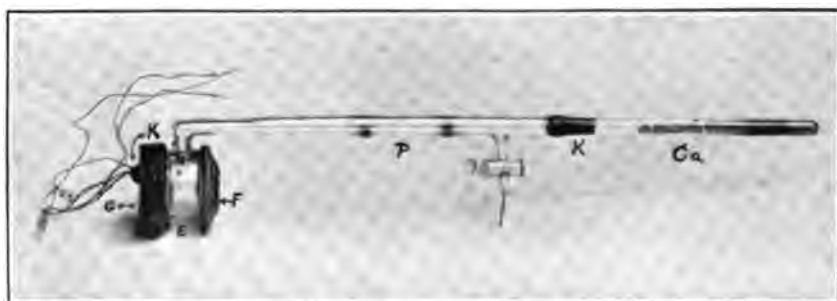


FIG. 3.—*Stellar thermocouples mounted in an evacuated glass container*

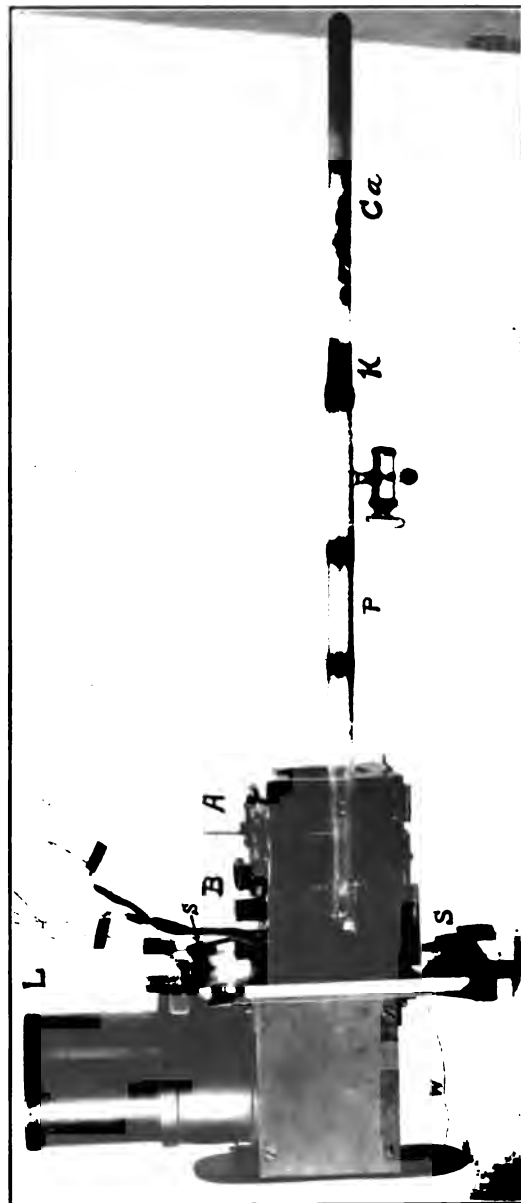


FIG. 4.—Stellar thermocouples, in glass container (see Fig. 3), mounted in viewing attachment of the Crossley reflector

3. THE METHOD USED FOR MAINTAINING A VACUUM

One of the difficulties with vacuum radiometers is that they can not be evacuated and sealed permanently, because vapors are given off from the walls of the container and from the lampblack-absorbing surfaces. The vapors become disengaged slowly, so that in time the radiation sensitivity of the radiometer is reduced. Provision must therefore be made to remove these vapors as they become disengaged.

It is a well-known fact that metallic calcium, when heated, has the property of combining with all atmospheric gases except argon. The application of this property of metallic calcium as an evacuator has been suggested as a result of the researches made by Moissan¹⁶ and by Arndt¹⁷. Experiments on the production of high vacua by means of metallic calcium have been made by Soddy¹⁸. A summary of the results of these experiments may be found in Baly's "Spectroscopy."¹⁹

In preparing the receptacles for the thermoelements shown in Fig. 3, the main difficulty experienced was in producing an air-tight container. This required so much time that, starting with the general information that calcium is useful in producing a vacuum, the application of this material for maintaining a vacuum in the present apparatus was perfected independently of previous work. In fact, the paper by Soddy was not consulted until after arrival on Mount Hamilton. This no doubt was a fortunate procedure, for some of the results obtained in the use of calcium as an evacuator seem to be at variance with previous experiments, and also at variance with the prevailing notion that calcium very readily attacks quartz. For example, it was found that a light-walled, quartz-glass tube could be used to contain the metallic calcium as shown in Fig. 3, *Ca*. This tube can be attached to the apparatus by means of Khotinsky cement, *K*, and heated to a low red heat without danger of cracking or collapsing when evacuated. At this temperature the metallic calcium unites readily with the residual gases without attacking the quartz-glass tube.

¹⁶ Moissan, *Compt. Rend.*, 127, pp. 29, 497, 584; 129, p. 1757; 1898.

¹⁷ Arndt, *Ber. d. Deutsch. Chem. Gesell.*, 37, p. 4733; 1904.

¹⁸ Soddy, *Proc. Roy. Soc.*, 78, p. 429; 1907.

¹⁹ Baly, *Spectroscopy*, p. 433 (edition 1912).

If heated to a bright red temperature, the hydrides and nitrides of calcium are dissociated and gases are evolved. On cooling, these gases again combine, and on admitting a small amount of air through the stopcock it was found that nitrogen, etc., continued to combine with the calcium until the temperature had fallen to about 300° . If the calcium is heated to a very bright red, then it, of course, combines chemically with the quartz glass. However, by evacuating the air to a pressure of about 0.1 millimeter there is no necessity for heating the calcium to a higher temperature than that indicated by the red glow of the quartz-glass tube. Porcelain tubes were also found satisfactory, but they are much heavier. The quartz-glass tubes were 8 millimeters in diameter, the thickness of the material being about 0.6 millimeter. In practice it would be better to use heavier material which is less fragile.

Before closing the container permanently it was found best to evacuate the air to a low pressure and heat the calcium to a bright red, which dissociates the hydrides, etc. The pumping is continued, and air is admitted repeatedly to assist in clearing the water vapor from the walls of the receptacle. Some of the air admitted combines, of course, with the hot calcium, but this is not detrimental. The quartz-glass tube may become black from the vaporized calcium, as shown in Fig. 3 (this is container No. 7, described on a previous page), but that seems to be beneficial rather than detrimental. In fact, the calcium in container No. 6 was not given this severe preliminary heating before detaching it from the pump, and the best vacuum was produced only after some of the calcium had been vaporized by a subsequent heating to a bright red. The black deposit on the walls of the quartz-glass tube is easily removed by means of soap and water.

The slight amount of vapors which were given off by the stopcock grease and the Khotinsky cement were removed by heating the calcium by means of an alcohol blast lamp, which was the most convenient method of heating on the mountain. A small electric heater, surrounding the quartz tube, might be provided in a permanent laboratory equipment. Now that the device has been shown to be useful, it is possible to eliminate the stopcock, thus removing one source of possible leaking. However, the stopcock

is the most useful part of the apparatus in case of any breakage, and it is not detrimental to retain it.

The two receptacles (Nos. 6 and 7, just described) were evacuated, the stopcocks were secured with Chatterton compound, and the vacuum was thereafter maintained by warming the metallic calcium, *Ca*, by means of either a small alcohol blast lamp or an ordinary wick alcohol lamp. This outfit was taken to Mount Hamilton, Cal., a distance of about 3,200 miles, without serious mishap. One element in No. 6 was broken in climbing the mountain, as already mentioned. In order to maintain uniformity of evacuation throughout the work the calcium was heated with the alcohol blast lamp several hours before beginning observations.

Some time after arrival on Mount Hamilton one of the receptacles began to leak a little. This was remedied by applying a coat of shellac to the ground joints. A vacuum pump was taken along to be used in case of serious accidents to the vacuum apparatus, but it was never unpacked. From this it is evident that, equipped with a number of evacuated receptacles, containing thermocouples, one can go to the remotest station to make radiometric measurements without being obliged to carry an expensive pump. This is one of the principal achievements in connection with the work.

The stopcock grease used was a haphazard combination of beeswax and mutton tallow (which was too hard for frequent turning of the stopcock), to which had been added a combination of rubber dissolved in vaseline. The latter when used alone was too soft to withstand the pressure upon the stopcock. The whole was heated in vacuo to remove the air and happened to be an excellent mixture. The Chatterton compound gave off vapors and hence was used only as an outside cover, because of its pliability when subjected to slow changes by expansion and contraction. As already mentioned, there seemed to be no leaking of air, and the vapors released from within were easily removed by warming the calcium. If the receptacles had leaked, all the constituents of the air could have been removed except argon, of which there would have been an accumulation which eventually would have been sufficient to reduce the radiation sensitivity of the thermoelements. Judging from the faint bluish discharge in container No. 6 when operated

on an induction coil, there was present a small amount of argon introduced by a temporary leakage, as already mentioned.

As to the actual degree of evacuation attained, no exact measurements were made. It was found that after warming the calcium the discharge from a 10 000 volt transformer could not be passed through the tube. At Mount Hamilton the tests were made with a small induction coil operated by two "dry batteries." In this test the discharge would pass through the 5 cm air space between the electrodes, *P*, Fig. 3, in preference to passing through the evacuated space within the tube. With reference to the efficiency of the device it may be added that this evacuator, employing calcium to maintain a vacuum, was found superior in operation to the carbon electrode evacuator described by Pfund.²⁰ In the latter it was found that, if the discharge was too vigorous, gases would be expelled which could be removed only by pumping, or by heating the calcium evacuator, which was tested at the same time. On the other hand, if the calcium be overheated, thus dissociating the hydrides, etc., the gases are again combined on cooling. The calcium evacuator is evidently useful in various researches where it is desired to maintain a high vacuum. The device is very simple in comparison with the apparatus used by Soddy.

4. THE REFLECTING TELESCOPE

The telescope used in this investigation is the well-known Crossley reflector, which is part of the equipment of the Lick Observatory at Mount Hamilton, Cal. The mirror has a focal length of 534 cm and a clear aperture of 92 cm, affording a ratio of aperture to focal length of 1 to 5.8. The support for the plate holder is 21 cm in diameter. In other words, the central portion of the reflector, about 21 cm in diameter, is shadowed by the plate holder and cuts out about 5 per cent of the light. The four webs which support the plate holder also cut out some light, so that the effective area exposed is about 6300 cm.² The mirror was in good condition, but removing the dust and polishing it greatly increased the galvanometer readings.

The reflector is situated at an altitude of about 4000 feet (1230 m), and the climatic conditions are excellent for making quan-

²⁰ Pfund, *Phys. Z. S.*, 18, p. 870; 1912.

titative measurements. The present investigation was made during the month of August. It was found that after sunset the wind would go down to a gentle breeze. For several nights in succession there would be no clouds, although to an experienced astronomer it would appear "hazy" and "poor seeing." The hygrometer would drop gradually from about 50 in the afternoon to as low as 10 per cent at 11 to 12 p. m. The summer months being rainless, there being no fog or dew, the night temperature being only a few degrees lower than the daytime, etc., were items which made it possible to have fairly uniform conditions on different nights. As will be shown presently, slight changes in humidity were easily observed. If the observations had been made in a more humid climate, it is possible that some of these small variations would have escaped detection. Before going to Mount Hamilton the plan was to use stars as standards of radiation to check the variation in radiation sensitivity of the thermocouples. After arrival at the observatory it was found that the radiation sensitivity of the elements was fairly constant, so that one of the problems was the observation of the variation of radiation from a star with variation in humidity.

On several nights, especially on August 17, the humidity was so low that every movement of the observer produced sufficient electrification to affect the galvanometer. It was necessary for the operator at the telescope to stand still while the galvanometer deflection was being observed. It was necessary also for the observer at the galvanometer telescope to sit in a fixed position while making an observation. For example, lifting the hands from the table which supported the reading telescope would cause a throw of 5 to 10 mm (or even several centimeters) of the galvanometer needle. However, this difficulty was very marked on only one night.

5. THE METHOD OF MAKING OBSERVATIONS

It may be added that the method of observation consisted in throwing the star image on or off the radiometer receiver by turning the declination slow-motion screw. This was done by the observer who operated the reflector. When the deflections were large the procedure was sometimes to expose the receiver to the star, and, at the signal "off" from the observer at the gal-

vanometer telescope, the operator tilted the telescope a slight amount to throw the star off the receiver. The usual procedure was to take the galvanometer deflections in rapid succession for the "on" and "off" readings. This was easier than to attempt to expose both receivers to the star, which would have doubled the deflection. On several nights everything was perfectly quiet, and it was wind-still, so that the galvanometer was steady to 0.1 mm. On those nights the greatest number of stars were observed. Momentary disturbances would, of course, occur and then no observations were taken. From 5 to 27 observations were recorded and the mean taken, which is given in the appended tables, with the maximum deviation of a single deflection from the mean value.

The maximum deviation from the mean frequently is larger for large deflections than for small ones. This is partly owing to the fact that less care was taken in reading large deflections than small ones. The measurement of blue stars became a task that was dreaded because of the small deflections. On several occasions it was windy at the start, or it became windy for a short time during the observations, which decreased the accuracy of the work. More difficulty was experienced in measuring the bright stars in the "Great dipper" than the red stars of smaller magnitude in the constellation Draco. As already stated, when the telescope was directed north of the zenith the lower end came close to the galvanometer, which was then affected by the rotation of the telescope tube. Hence, only a few stars north of the zenith were measured.

6. SENSITIVITY TESTS ON STARS

The sensitivity of these thermocouples was tested by means of an artificial star, and also when they were mounted in the telescope and exposed to a star such as Vega. It was found that the radiation sensitivity of the two thermocouples in No. 7 (1, bismuth-bismuth and tin alloy; 2, bismuth-platinum) differed but little in spite of the fact that the one containing the bismuth-tin alloy had a 50 per cent higher thermoelectric power. The best receiver, 1a (Bi-BiSn; 0.38 mm in diameter), was perhaps 10 per cent more sensitive than the others in container No. 7.

This receiver, recorded as No. 7 (*1a*) in the appended tables, was therefore used for most of the work (until the quartz tube containing the calcium was broken), owing to the fact that container No. 6 appeared to leak slightly at the start, and hence was not used for fear of a variation in its radiation sensitivity.

In container No. 6, three of the receivers (*1a*, *1b*, and *3a*) had practically the same radiation sensitivity when exposed to Arc-turus. The best receiver, *3b*, was from 30 to 40 per cent more sensitive than the others, and it was perhaps 25 per cent more sensitive than the best receiver (*1a*) in container No. 7. Similar tests made in the laboratory, using an artificial star, showed that, with the exception of the receiver *3b*, all the receivers had closely the same sensitivity. The greatest uniformity in sensitivity in different thermoelements was obtained with bismuth and platinum. The lack of uniformity in sensitivity of thermocouples containing bismuth-tin alloy is no doubt owing to the difference in the size of the material used. For example, in the most sensitive junction, No. 6 (*3b*), the cross section of the strip of bismuth-tin alloy was smaller than that of the strip of alloy which was attached to the junction, No. 6 (*3a*). Evidently the decrease in heat capacity, and especially heat conductivity, increased the sensitivity of the junction No. 6 (*3b*).

It was the intention to construct and test the sensitivity of various designs of thermocouples and mount the most sensitive ones in the glass containers. However, so much time was required in designing a container which would not leak that but little time was left for constructing thermocouples. Those just described were selected from about a dozen thermocouples. The elements of bismuth-silver were only half as sensitive as the ones of bismuth-platinum. This no doubt is attributable to the low heat conductivity of the platinum wire, for its thermoelectric power is but little higher than that of silver.

It might be added that the great difference in sensitivity of the receivers attached to the thermocouple No. 6 (*3a*, *3b*) produced a permanent deflection when the galvanometer circuit was closed. This, however, caused no inconvenience in making the galvanometer readings, for the galvanometer suspension was sufficiently steady, so that observations could be made with a 20-mile per

hour wind blowing into the dome and upon the radiometric apparatus. In fact, some measurements were made in the southeastern sky when a very strong northwest wind was blowing. The receivers being small, the difference in their size and their emissivity has but little effect upon the steadiness of the galvanometer.

7. SENSITIVITY TESTS BY MEANS OF A CANDLE

The intercomparison of stellar radiometers and the determination of the sensitivity of these thermocouples by means of the radiation from a candle has but little meaning in the present work. The diameters of the receivers used were only one-third to one-sixth that of the radiometers previously employed. This means that the candle tests of the instruments previously employed would indicate a sensitivity (which varies as the square root of the area) of four to six times that observed with the present instruments. Nevertheless, the receivers used in the present investigation were sufficiently large to take in practically all the energy in the stellar diffraction rings that would be of importance theoretically, while in practice they included all the light visible even from the brightest stars.

The significant point in any discussion of the sensitivity of the apparatus is the work that was accomplished. This is the main thing that counts, and on this basis we have the following facts for consideration. The Nichols radiometer when combined with a 2-foot mirror and exposed to several of the brightest stars gave a series of positive and negative deflections, the mean of which gave a positive result. As a piece of pioneering work it stands pre-eminent, but when one considers how much depends upon the sensitivity of the radiometer and how little is gained by using a large mirror, it appears that this form of radiometer has but little to contribute by way of further improvement.

With the present outfit it was possible to measure the radiation from stars down to the six and seven-tenths magnitude with as great a degree of certainty as was attained in previous measurements on such stars as Arcturus. In other words, with the present outfit stars were measured which were $1/400$ to $1/500$ as bright as those formerly measured, or the sensitivity was 400 to 500 times as great as was previously attained. Of this total gain in sensitivity, part

was due to a decrease in atmospheric absorption, and part was due to the use of a 3-foot mirror, which took in about 2.3 times as much stellar radiation as was obtained by Nichols. This places the sensitivity of the radiometer itself at about 200 times that previously used.

The sensitivity of receiver No. 6 (3b) was tested with a sperm candle at a distance of 3.2 m. The deflection was 101 mm for a galvanometer sensitivity of $i = 1 \times 10^{-10}$ ampere, or 1040 mm for a candle at 1 m. This, of course, should be increased by about 10 per cent to correct for absorption and reflection by the fluorite window. The diameter of the receiver was about 0.335 mm, giving a total area of exposed surface of about 0.089 mm². The ratio of the receiver to the effective aperture of the mirror is approximately 0.089:630 000. Hence, the corresponding deflection for the total radiation from a candle incident upon the concave mirror used (the candle being at a distance of 1 m from the mirror) would be equivalent to $1040 \times 7\ 100\ 000 = 7\ 400\ 000\ 000$ mm. In other words, using this radiometric outfit, the total radiation received from a star giving 1 mm deflection is about 1/7 400 000 000 that of a candle at 1 m. The deflection caused by Arcturus was 84 mm. Hence, in terms of the candle test, the total radiation received from Arcturus is somewhat greater than the 1/100 000 000 part of the radiation from a candle at a distance of 1 m. Nichols observed practically this same value of the radiation from Arcturus in terms of the candle, the actual deflection observed being, of course, very much smaller, viz, about 0.5 mm.

In regard to the sensitivity of the apparatus, the candle test signifies that (assuming, of course, that there is no absorption in passing through the intervening space) if the image of the flame were focused upon the receiver of this thermocouple by means of a 3-foot reflecting telescope, a deflection of 1 mm would be observed if the candle were placed at a distance of about 53 miles. This value seems preposterous, but it is in agreement with the data published by Nichols. His aperture ratio was 1:94 968, which was equivalent to a deflection of 68 750 000 mm. In other words, his radiometer combined with his 2-foot mirror would have given a deflection of 1 mm when the candle was placed at a distance of 5 miles. The present aperture ratio was almost 110 times

as great, so that on this basis alone it would be possible (assuming the same radiometer sensitivity used by Nichols) to remove the candle to 10 times the distance, viz, 50 miles. With Pfund's apparatus a deflection of 1 mm would have resulted if the lamp had been removed to a distance of about 8 miles. This estimate seems to be low. A computation of the data given by Pfund makes this distance about 19 miles.²

To be entirely fair in making a comparison of the present instrument with the Nichols radiometer, allowance should be made for the gain in radiation by a diminution of the scattering and absorption of stellar radiation, which was brought about by making the observations at a high altitude. This might reduce the actual sensitivity of the thermocouples and auxiliary galvanometer to about 150 times that of the Nichols radiometer. It is to be borne in mind, however, that the Nichols radiometer had been worked quite close to the limit both as regards period and stability (weight of suspension) so that there was but little to be expected by way of further increase in its sensitivity. On the other hand, the sensitivity of the galvanometer used in the present measurements could easily have been increased 10 times; while it is the hope of some experimenters to increase the sensitivity of the auxiliary galvanometer to 50 times that used in the present work. In fact, such an increase in sensitivity will be necessary in order to be able to do much work on spectral-energy curves of stars; for the gain in stellar radiations collected by the largest mirror is not at all commensurate with what is needed for successful measurements.

By using the largest mirror available, from 3 to 6 times as much light would be intercepted as was possible with the present apparatus. This signifies galvanometer deflections of 2 to 10 cm (as may be noticed in the appended tables), which is not a great gain. In order to obtain a good spectral-energy curve it will be necessary to magnify these deflections by 50 to 100 times; and the burden will evidently fall upon the radiometric part of the equipment. Hence, while it may be gratifying to contemplate what was accom-

² A letter from Dr. Pfund states the distance to be 18.6 miles, the former value being a typographical error.

plished with the present equipment, it is but a small stride in advance in comparison with what will be necessary in order to observe the spectral-energy curves of a few of the countless number of stars which are visible on a clear night. The present work signifies that to measure the spectra of the brightest stars it is desirable to have a sensitivity 100 times that used on Mount Hamilton; or, in terms of the candle test, a deflection of 1 mm would be observed from a candle placed at a distance of 500 miles. This can be accomplished by using a 7-foot reflector and by increasing the radiometer sensitivity 20 times. The radiometer sensitivity may be increased 20 times by increasing the radiation sensitivity of the thermocouple 2 times and the sensitivity of the auxiliary galvanometer 10 times (i. e., to $i = 1 \times 10^{-11}$ ampere). The sensitivity of the latter may be increased by increasing the period and by placing the instrument in a vacuum. Other work will of course be possible with a far less sensitive radiometric equipment, the most conspicuous being measurements of variable stars.

TABLE 1

Showing the Number of Stars of Each Magnitude and the Brightness of the Star as Compared with a Star of Zero Magnitude

Magnitude	Number of visible stars	Brightness	Magnitude	Number of visible stars	Brightness
0	6	$\frac{1}{1}$	4	500	$\frac{1}{39.8}$
1	20	$\frac{1}{2.5}$	5	1400	$\frac{1}{100}$
2	60	$\frac{1}{6.25}$	6	5000	$\frac{1}{252}$
3	200	$\frac{1}{15.9}$	7	20000	$\frac{1}{631}$

In connection with the forgoing discussion, Table 1 is of interest in showing the number of available stars of each magnitude, and the rapid decrease in brightness with magnitude. On a subsequent page it will be shown that there is a close relation between photometric brightness and the total radiation from different classes of stars.

8. COMPARISON OF THE RADIATION SENSITIVITY OF A BOLOMETER AND A THERMOELEMENT

Time did not permit the construction of stellar bolometers, as had been planned, to compare (on Mount Hamilton) with the stellar thermocouples. The proposed design of the bolometer which was to be tested is shown in Fig. 2. From the tests made in the laboratory, using an artificial star, and from the tests of vacuum bolometers by Buchwald,²² it does not appear that the radiation sensitivity of a vacuum bolometer can be made very much higher than that of the herein-described vacuum thermocouples. The radiation sensitivity of these thermocouples is increased about 4.5 times by evacuating the air, as described. This is practically the same as Buchwald observed with a vacuum bolometer. Similar results were obtained by Warburg²³ and his associates who found that a vacuum bolometer 0.2 mm wide was 10 times as sensitive as it was in air, when used on a small current; but it was only 5 times as sensitive when, in both cases, the current was raised to its highest operating value.

It is doubtful whether as high a bolometer current can be used in an open dome as in a closed laboratory, so that on the basis of these tests the gain in sensitivity is probably 4 to 5 times that observed in air. The thermocouple is no doubt the least affected by wind and by temperature variations, so that, even though it may be less sensitive than the bolometer, it will be the steadier in its behavior when connected with the auxiliary galvanometer. It will therefore be possible to read smaller deflections with the thermocouple.

The present sensitivity comparisons were made on one of the bolometers in regular use in this laboratory.²⁴ The instrument "No. 10" is considered a very good one. In an investigation of the spectral-energy curves of a black body²⁵ it was found that this bolometer had practically the same sensitivity as the linear thermopiles²⁶ of bismuth and silver. An estimate of the relative merits of the stellar thermoelements and a bolometer may therefore be obtained (1) by comparing the sensitivity per unit

²² Buchwald, *Ann. der Phys.* (4), 25, p. 928; 1910.

²³ Warburg, Leithauser, and Johansen, *Ann. der Phys.*, (4), 24, p. 25; 1907.

²⁴ This Bulletin, 9, p. 39; 1911.

²⁵ This Bulletin, 10, p. 2; 1913.

²⁶ This Bulletin, 11, p. 131, 1914.

area of the linear thermopiles with the stellar thermocouples, and (2) by comparing the latter with the bolometer by exposing them to the radiation from an artificial star.

The star used was simply a hole about 0.1 mm in diameter punched into a thin sheet of copper, back of which was a cylindrical acetylene flame. An image of this artificial star was projected upon the radiometer receiver by means of a triple achromatic lens, 6 cm in diameter and 18 cm in focal length. In both instruments the star image was intercepted entirely by the receiver.

The thermoelement, No. 6 (3b), when exposed to the radiation from this star, gave a deflection of 152 mm, while the receiver No. 6 (3a) gave a deflection of 112 mm. The bolometer in air on 0.04 ampere, when exposed to this star, gave a deflection of only 10 to 11 mm, which would amount to about 40 to 50 mm in a vacuum. From previous experience it did not appear that the bolometer current could be increased much above 0.04 ampere. This test, therefore, shows that the best thermoelement was from three to four times as sensitive as the bolometer.

That the intrinsic sensitivity of the stellar thermojunction is much higher than that of a linear thermopile (and hence a bolometer as just mentioned) is shown from the following test in which the source of energy was a standard of radiation²⁷ in the form of an incandescent lamp. A linear thermopile of bismuth-silver (No. 36; exposed surface 17.3 by 1.8 mm) gave a deflection of 445 cm for a galvanometer sensitivity of $i = 1 \times 10^{-10}$ ampere. This is equivalent to about 79 cm deflection per mm² of exposed surface of the receiver. This value would be increased about two times (=158 cm) if the thermopile were in an evacuated container. The stellar thermoelement No. 6 (3b) gave a deflection of 59 cm, which, when corrected for reflection from the fluorite window, amounts to about 65 cm for a galvanometer sensitivity of $i = 1 \times 10^{-10}$ ampere. The area of this receiver was 0.089 mm². Hence for a receiver having an exposed area of 1 mm² the deflection (which varies as the square root of the area) would have been 3.5 to 4 times this value, or 225 to 260 cm. In other words, the receiver of the stellar thermojunction used in this work is 1.5 to 2 times more sensitive than the receivers in a linear thermopile.

²⁷ This Bulletin, 11, p. 87, 1914.

Further tests of new bolometers and thermocouples must of course be made; but, from the evidence now available, it appears that a greater advance is to be expected in a further improvement of thermoelements than in a further improvement of the bolometer.

IV. MEASUREMENTS OF THE TOTAL RADIATION FROM STARS

Under this title are discussed some of the results of the radiometric measurements of stars given in Table 2. (The time given is Pacific Standard time.) In all 112 celestial objects were measured, of which number 105 were stars, which varied in brightness down to magnitude 6.66. It was simply a question of time and physical endurance, in order to extend the work. If this had been merely an attempt to show the possibilities of the instruments then, by increasing the galvanometer sensitivity, positive indications could have been obtained of radiation from red stars down to the eighth or perhaps the ninth magnitude. That, however, would have been simply a spectacular achievement, to awe the layman, and under the present conditions of observation could not have contributed much to science.

Stars fainter than the sixth magnitude were difficult to project upon the receiver of the thermocouple, while blue stars fainter than the fourth magnitude were rather instinctively avoided, owing to the weakness of their total radiation.

It is impossible to give in detail the conditions under which the observations were made. For example, late at night on August 8 the observations were discontinued on account of the presence of a light haziness and cloudiness, which, if there had been no moonlight, could not have been seen. The observations on August 13 were affected by light clouds, and had to be repeated. They are very instructive, however, in showing how seriously the total radiation is affected by light clouds. It is difficult to describe the nature of these clouds. They are "thin," diaphanous formations, and on this occasion it was particularly noted that the two fainter stars in the triangle of the constellation Lyra were still visible through the cloud formation. Nevertheless, the observed deflection for Vega was only 1.26 cm, which is only 0.36 of the value usually observed.

August 12 is recorded as the best night experienced. This refers to freedom from wind, excellence in galvanometer behavior, etc. Occasionally temporary difficulties would be experienced at the beginning of a series of observations. For example, on August 26, when observations were begun at midnight, there was a high northwest wind, and the galvanometer drifted seriously while making measurements on stars in the constellation Perseus. Within an hour the wind had subsided and excellent work could be done until dawn.

TABLE 2

I. Thermoelement No. 6 (3b)

Date	Hour	Object	Magni- tude	Ob- served deflec- tion	Maxi- mum devia- tion from mean value	Galvanom- eter sensi- tivity $I = x \times 10^{-10}$ amp.	Galva- nomet- er deflec- tion for $I =$ 1×10^{-10} amp.	Deflec- tion re- duced to sen- sitivity of July 30	Class of star
1914				cm		$I =$		cm	
July 30	9.30	α Boötis.....	0.24	6.48	0.07	1.31	8.49	8.58	K
				7.55	.10	1.15	8.66		
Aug. 3	9.20			8.35	.15	1.02	8.35	8.58	
				.65	.08	9.45×10^{-11}	.61		
July 30	10.00	α Ophiuchi.....	2.14	.21	.03	3.13	.66	.64	A 5
				.34	.04	1.88	.64		
July 30	10.30	α Lyrae.....	.14	2.14	.08	1.67	3.54	3.54	A
July 30	10.50	α Aquilae.....	.89	1.15	.07	1.64	1.89	1.89	A 5
Aug. 1	11.45			.53+	.08	1.74	.93	1.89	
July 30	11.15	Jupiter, bright band....		3.6	.10	1.61	5.8	5.8	
July 30	11.45	Jupiter, dark band....		2.6	.10	1.61	4.2	4.2	
July 30	11.45	Jupiter; 2 satellites....		.03-.07		1.61	$1 \pm$	$.2 \pm$	
Aug. 1	8.15	Venus.....		22.1	.15	1.45	33.0+	70.0+	
Aug. 1	8.40	Mars.....		.35-.40	.10	1.2	.45	.90+	
Aug. 1	10.30	α Scorpii.....	1.22	4.7	.10	1.01	4.8+	9.6+	Mag
Aug. 1	11.40	γ Aquilae.....	2.80	.16	.04	1.80	.29	.58	K 2
Aug. 1	9.30	Planetary nebula, N. G. C. 6572.		$\pm .02$		1.10	$\pm .02$		

II. Thermoelement No. 7 (1a)

Aug. 3	10.40	γ Cygni.....	2.32	0.38	0.07	1.16	0.44	0.47	F 8 p
Aug. 3	11.20	α Pegasi.....	2.57	.22	.04	1.39	.29	.31	A
Aug. 3	12.20	ε Pegasi.....	2.54	.65	.06	1.19	.77	.82	K
Aug. 4	9.00	α Virginis.....	1.21	.2+		1.2			B 2
Aug. 4	9.30	α Boötis.....	.24	5.36	.07	1.37	7.35	8.58	K
Aug. 4	10.10	α Coronae Borealis.....	2.31	.34	.04	1.36	.46	.54	A 0
Aug. 19	8.15			.30	.02	1.60	.48		
Aug. 4	10.30	α Serpentis.....	2.75	.37	.05	1.42	.53	.62	K

TABLE 2—Continued

II. Thermoelement No. 7 (1a)—Continued

Date	Hour	Object	Magni- tude	Ob- served deflec- tion	Maxi- mum devia- tion from mean value	Galvanom- eter sensi- tivity $i = x \times 10^{-10}$ amp.	Galvanom- eter def- lection for $i =$ 1×10^{-10} amp.	Deflec- tion re- duced to sen- sitivity of July 30	Class of star
1914				cm		$x =$		cm	
Aug. 4	10.50	β Ophiuchi.....	2.94	0.30	0.06	1.23	0.37	0.43	K
Aug. 19	8.15			.22	.03	1.69	.37		
Aug. 4	11.15	ζ Aquilae.....	3.02	.21	.04	1.14	.24	.28	A
Aug. 4	11.45	ϵ Cygni.....	2.64	.46	.06	1.09	.51	.60	K
Aug. 4	12.25	γ Pegasi.....	3.10	.30	.05	9.5×10^{-11}	.29	.34	G
Aug. 4	13.00	β Pegasi.....	2.61	2.58	.06	9.8×10^{-11}	2.54	2.96	M 6
Aug. 4	13.55	γ Pegasi.....	2.87	.18	.05	1.57	.28	0.33	B 2
Aug. 4	2.20	α Andromedae.....	2.15	.22	.06	1.57	.35	.41	A 0
Aug. 8	8.45			.64	.05	1.64	1.05	1.33	
	10.40	α Ursae Majoris.....	1.95	.44	.04	1.88	.83	1.05	K
Aug. 8	9.25	β Ursae Majoris.....	2.44	.20	.06	1.48	.29	.37	A
Aug. 8	9.45	γ Ursae Majoris.....	2.54	.15	.03	1.46	.22	.27	
				.19	.04	1.15	.22		A
Aug. 8	10.20	ϵ Ursae Majoris.....	1.68	.31	.05	2.18	.67	.85	A p
Aug. 8	11.10			.67	.03	1.85	1.24	1.58	
Aug. 9	12.20	γ Draconis.....	2.42	.59	.04	2.25	1.32	1.67	K 5
Aug. 12	8.45			.60	.05	2.15	1.29	1.64	
Aug. 8	11.35	δ Draconis.....	3.24	.20	.02	1.73	.45	.57	K
Aug. 8	12.00	ϵ Draconis.....	3.99	.08-.10	.03	1.70	10-.15	13-.19	K
Aug. 8	12.35	α Cygni.....	1.33	.68	.04	1.69	1.16	1.47	A 2
Aug. 8	12.50			1.65	.06	1.66	2.75	3.50	
Aug. 12	9.10	α Lyrae.....	.14	1.34	.04	2.08	2.79	3.54	A
Aug. 9	9.10	γ Ursae Majoris.....	1.91	.29	.03	1.72	.50	.64	B 3
Aug. 9	9.50	β Ursae Minoris.....	2.24	.47	.05	1.61	.76	.97	K 5
Aug. 9	10.30	α Ursae Minoris.....	2.12	.23	.05	2.02	.47	.60	F 8
Aug. 9	11.10	α Cassiopeiae.....	2.3-2.8	.22	.05	2.03	.45	.57	K
Aug. 9	11.25	β Cassiopeiae.....	2.42	.13	.03	2.06	.27	.34	F 5
Aug. 9	11.50	γ Cassiopeiae.....	2.25	.12	.03	2.03	.24	.31	B p
Aug. 12	9.35	β Draconis.....	2.99	.18	.04	1.92	.35	.44	O
Aug. 12	10.00	γ Draconis.....	2.89	.26	.04	1.95	.51	.65	O 5
Aug. 12	10.20	ζ Draconis.....	3.22	.11	.03	2.25	.25	.32	B 5
Aug. 12	10.45	δ Draconis.....	3.24	.17	.03	2.30	.39	.50	K
Aug. 12	11.15	H. R. 7676 Draconis...	5.43	.05	.02	2.38	.12	.15	M a
Aug. 12	11.35	β Cephei.....	3.32	.10	.02	2.15	.22	.28	B 1
Aug. 12	12.35	β Andromedae.....	2.37	.82	.04	2.14	1.75	2.23	M a
Aug. 12	13.10	γ Andromedae, star A.	2.20	.49	.05	2.24	1.10	1.40	K p
Aug. 12	13.30	γ Andromedae, star BC	5.08	.04	.02	2.24	.09	.11	Blue
Aug. 13	8.55	ϵ Boötis.....	2.70	.34	.02	1.72	.59	.83	K
Aug. 13	9.15			3.47	.08	1.77	6.14	8.58	
Aug. 17	9.00	α Boötis.....	.24	5.27	.06	1.62	8.53	8.53	K
Aug. 13	9.30			.14	.04	1.95	.27	.38	
Aug. 15	9.15	ϵ Ophiuchi.....	3.34	.16	.03	2.07	.33	.48	K

a Clouds.

TABLE 2—Continued

II. Thermoelement No. 7 (1a)—Continued

Date	Hour	Object	Magni- tude	Ob- served deflec- tion	Maxi- mum devia- tion from mean value	Galvanom- eter sensi- tivity $1-x \times 10^{-10}$ amp.	Galva- nometer deflec- tion for $1-1 \times 10^{-10}$ amp.	Deflec- tion re- duced to sen- sitivity of July 30	Class of star
1914				cm		$x=$		cm	
Aug. 13	9.45	δ Ophiuchi.....	3.03	0.20	0.04	2.04	0.41	0.58	M a
Aug. 15	8.50			.37	.05	2.16	.80	1.16	
Aug. 19	8.50			.74	.04	1.85	1.37	1.37	
Aug. 13	10.20	α Herculis, star A.....	3.48	2.15	.07	2.20	4.73	6.61	M b
Aug. 15	9.30			2.08	.03	2.18	4.55	6.60	
Aug. 16	11.30			2.66	.05	1.70	4.53	5.81	
Aug. 17	12.00	α Herculis component.....	5.39	4.45	.08	1.52	6.78	6.78	Blue
Aug. 13	10.20			.49	.05	2.20	1.1	1.54	
Aug. 15	9.30			.41	.05	2.18	.90	1.31	
Aug. 13	10.45	β Herculis.....	2.81	.17	.04	2.01	.34	.48	K
Aug. 13	11.05	γ Herculis.....	3.00	.12	.04	1.98	.24	.34	G
Aug. 15	9.45			.14	.03	2.15	.30	.44	
Aug. 13	11.20	ε Herculis.....	3.92	.05	.03	1.98	.10	.14	A
Aug. 13	12.00	α Lyrae.....	.14	.66	.06	1.91	1.26	(b)	A
Aug. 15	10.20			1.24	.10	1.95	2.42	3.53	
Aug. 16	11.40			1.58	.05	1.76	2.78		
Aug. 17	12.45			1.92	.06	1.69	3.25		
Aug. 15	10.00	δ Herculis.....	3.16	.11	.03	2.15	.23	.33	A
Aug. 15	11.20	β Aquilae.....	3.90	.12	.03	1.74	.21	.30	K
Aug. 15	11.50	β Cygni, star A.....	3.24	.18	.03	1.93	.35	.50	K p
Aug. 15	11.50	β Cygni component.....	5.36	.03	.02	1.93	.05-.06	.07-.09	Blue
Aug. 15	12.20	α Aquilae.....	.89	.59	.07	1.96	1.17	1.68	A 5
Aug. 16	10.55			.69	.04	1.67	1.15	1.28	
Aug. 17	9.50			1.38	.05	1.37	1.89	1.89	
Aug. 16	8.30	δ Aquilae.....	3.44	.17	.04	1.65	.23	.30	F
Aug. 16	8.50	θ Aquilae.....	3.37	.10	.04	1.67	.17	.22	A
Aug. 16	9.15	ε Aquarii.....	3.83	.05	.02	1.67	.08	.10	A
Aug. 16	9.40	δ Sagittae.....	3.78	.35	.03	1.71	.60	.77	M a p
Aug. 16	10.00	γ Sagittae.....	3.71	.23	.03	1.74	.40	.51	K 5
Aug. 16	10.15	ι Aquilae.....	4.28	.03	.02	1.74	.05	.06	B 5
Aug. 16	10.35	ε Aquilae.....	4.21	.13	.03	1.66	.22	.28	K
Aug. 16	11.20	μ Herculis.....	3.48	.19	.03	1.69	.32	.41	G 5
Aug. 16	11.30	α Herculis.....	c 3.48	2.66	.05	1.70	4.53	5.81	M b
Aug. 17	12.00			4.45	.08	1.52	6.78	6.78	
Aug. 17	9.30			8.56	.07	1.27	10.8	10.8	
Aug. 1	10.30	α Scorpii.....	1.22	4.7		1.01	4.8	49.6	M a p
Aug. 17	10.25	7680 Aquilae.....	6.36	.043	.02	1.34	.055-.06	.06	M a p
Aug. 17	11.15	Jupiter.....		5.50	.09	1.54	8.5	8.5	
Aug. 17	12.30	γ Draconis.....	2.42	.93	.05	1.71	1.59	1.59	K 5
Aug. 19	7.30	Venus.....		48.0	.08	2.64	127.	127.	
Aug. 19	8.15	α Coronae Borealis.....	2.32	.30	.06	1.60	.48	.48	A
Aug. 19	8.35	β Ophiuchi.....	2.94	.22	.04	1.69	.37	.37	K

A Light haze.

c Variable.

d Element No. 6.

TABLE 2—Continued

II. Thermoelement No. 7 (1a)—Continued

Date	Hour	Object	Magni- tude	Ob- served deflection	Maxi- mum devia- tion from mean value	Galvanom- eter sensi- tivity $i = x \times 10^{-10}$ amp.	Galva- nom- eter de- flection for $i = 1 \times 10^{-10}$ amp.	Deflec- tion re- duced to sen- sitivity of July 30	Class of star
1914				cm		$x =$		cm	
Aug. 19	8.50	δ Ophiuchi.....	3.03	0.74	0.04	1.85	1.37	1.37	M a
Aug. 20	8.50	β Librae.....	2.74	.16	.03	2.16	.34	.47	B 8
Aug. 20	9.00	δ Scorpii.....	2.54	.19	.03	2.04	.39	.54	B
Aug. 20	9.15	β Scorpii, star A.....	2.90	.11	.03	2.17	.24	.33	B 1
Aug. 20	9.15	β Scorpii component.....	5.06	.03	.02	2.17	.05-.06	.07-.08	Blue
Aug. 20	9.35	γ Serpentis.....	3.86	.12	.03	1.96	.23	.32	F 8
Aug. 20	9.45	α Serpentis.....	4.28	.21	.04	1.96	.41	.57	K 5
Aug. 20	10.00	ζ Sagittarii.....	2.70	.14	.03	1.69	.24	.33	A 2
Aug. 20	10.15	η Ophiuchi.....	2.63	.13	.03	1.71	.22	.30	A
Aug. 20	10.30	ϵ Ophiuchi.....	4.44	.15	.03	1.84	.27	.37	K
Aug. 20	10.50	6543 Ophiuchi.....	6.66	.04	.02	2.06	.08	.11	M b
Aug. 20	11.10	β Capricorni.....	3.25	.20	.03	1.78	.36	.50	G p
Aug. 20	11.20	β Aquarii.....	3.07	.22	.05	1.83	.40	.55	G
Aug. 20	11.30	δ Capricorni.....	2.98	.10	.02	1.99	.20	.28	A 5
Aug. 20	11.45	α Aquarii.....	3.19	.25	.02	1.99	.50	.69	G
Aug. 20	12.00	γ Aquarii.....	3.97	.08	.02	2.07	.17	.24	A
Aug. 20	12.10	λ Aquarii.....	3.84	.33	.03	2.21	.73	1.02	M a
Aug. 20	12.20	ζ Pegasi.....	3.61	.05	.02	2.17	.11	.15	B 8
Aug. 20	12.40	ζ Cygni.....	3.40	.21	.03	1.76	.37	.51	K
Aug. 20	13.10	α Lyrae.....	.14	1.50	.08	1.69	2.54	3.54	A
				1.06	.04	2.43	2.57		

III. Thermoelement No. 6 (3 b)

Aug. 24	12.30	α Lyrae.....	0.14	3.7	0.10	1.22	4.52	3.62	A
Aug. 24	13.15	β Pegasi.....	2.61	2.84	.05	1.19	3.39	2.71	M b
Aug. 24	13.45	ϕ Pegasi.....	5.23	.22	.04	1.26	.28	.22	M a
Aug. 24	14.05	H. R. 9004, 19 Piscium.....	5.30	.33	.05	1.78	.59		N
				.27	.02	2.02	.55	.46	
Aug. 24	14.35	α Piscis Australis.....	1.29	.56	.03	1.99	1.12	.90	A 3
Aug. 24	14.50	β Ceti.....	2.24	.52	.04	2.07	1.08	.86	K
Aug. 24	15.10	ν Ceti.....	4.18	.19	.03	2.03	.39	.31	M a
Aug. 24	15.40	δ Ceti.....	4.04	.05	.02	2.05	.10	.08	B 2
Aug. 24	15.50	α Arietis.....	2.23	.18	.02	2.43	.44	.35	K 2
Aug. 24	16.20	α Tauri.....	1.06	3.66	.04	2.31	8.46	6.78	K 5
Aug. 26	16.15			3.53		2.27	8.05	6.84	
Aug. 24	16.45	α Auriga.....	.21	3.32	.03	2.31	7.67	6.14	G
Aug. 26	12.45	γ Persei.....	3.08	.41	.02	2.04	.84	.72	G p
Aug. 26	13.00	δ Persei.....	3.10	.25	.03	2.08	.52	.44	B 5
Aug. 26	13.20	α Persei.....	1.90	.64	.05	2.54	1.63	1.38	F 5
Aug. 26	13.40	β Persei.....	2.1-3.2	.39	.05	2.32	.91	.77	B 8
Aug. 26	13.55	ζ Persei.....	2.91	.20	.03	2.31	.46	.39	B 1

TABLE 2—Continued

III. Thermoelement No. 6 (3b)—Continued

Date	Hour	Object	Magni- tude	Ob- served deflec- tion	Maxi- mum devia- tion from mean value	Galvanom- eter sensi- tivity $i = x \times 10^{-10}$ amp.	Galva- nome- ter def- lection for $i =$ 1×10^{-10} amp.	Deflec- tion re- duced to sen- sitivity of July 30	Class of star
1914				cm		$x =$		cm	
Aug. 26	14. 15	γ Tauri.....	3.86	0.18	0.02	2.35	0.42	0.36	G
Aug. 26	14. 35	δ Tauri.....	3.93	.25	.03	2.44	.61	.52	K
Aug. 26	14. 50	ν Tauri.....	3.94	.06	.02	2.24	.14	.12	A
Aug. 26	15. 05	ρ^a Tauri.....	3.62	.09	.03	2.28	.21	.18	A 5
Aug. 26	15. 20	ϵ Tauri.....	3.63	.17	.03	2.38	.41	.35	K
Aug. 26	15. 40	β Tauri.....	1.78	.49	.03	2.21	1.08	.92	B 8
Aug. 26	16. 15	α Tauri.....	1.06	3.53	.05	2.27	8.05	6.85	K 5
Aug. 26	16. 05	Saturn.....		.55	.05	2.34	1.29	1.10	
Aug. 26	16. 05	Saturn, rings.....		.28	.04	2.34	.66	.56	
Aug. 26	16. 25	α Orionis.....	.92	9.92	.07	2.27	22.52	19.14	M a
Aug. 26	16. 40	β Orionis.....	.34	1.42	.08	2.07	2.94	2.50	B 8 p
Aug. 26	17. 00	γ Orionis.....	1.70	.54	.04	1.98	1.07	.91	B 2
Aug. 27	7. 20	Moon.....		24.7	.2	3.40	84.	84.	

Occasionally a correction had to be made for the effect of tilting the telescope in observing the radiation from a star. The star ϵ Draconis (magnitude=3.99) is an excellent example. The mean value of 23 readings gave a value of 0.11 cm for the total deflection. From this had to be deducted 0.04 cm, which was the effect of tilting the telescope tube. This test for the effect of the movement of the telescope was made on all faint stars. The correction, if any, was never greater than 0.04 cm, and usually it was of the order of 0.01 to 0.02 cm.

As already mentioned, after the work was systematized, pairs of stars were selected which had closely the same magnitude, but differed in color. These data were obtained from the Harvard Revised Photometry, volume 50, recorded in the present paper as "H. R.," with the catalogue number of the star.

It will be too tedious to call attention to all the examples of pairs of stars differing in color, which demonstrate the great difference in the total radiation emitted. The reader is referred to the appended tables, especially to the pairs of stars observed at closely the same time, on the same night. It is desirable, however, to mention a few of the conspicuous stars, especially those familiar to

most readers. Take, for example, the bright stars in the "Big dipper." The yellow star in the "Pointers," α Ursae Majoris (magnitude = 1.95) is fainter to the eye than the blue star in the bend of the "handle," ϵ Ursae Majoris (magnitude = 1.68). Nevertheless, it was proven definitely that the total radiation emitted by the smaller, yellow, star is almost double that of the blue star. To make certain, the observations on α Ursae Majoris were repeated after it had sunken low on the horizon. Even then it emitted the more radiation. (See Table 2, "I. Thermoelement No. 6 (3b).") Another familiar constellation is Cassiopeiae. The star β Cassiopeiae, which is yellow, is fainter (magnitude = 2.4) than the blue star, γ Cassiopeiae (magnitude = 2.25). Nevertheless, the former emits the more energy. In the same manner it was found that the pole star, α Ursae Minoris, which is yellow, emits less total radiation than the fainter reddish yellow star, β Ursae Minoris in the "Little dipper," familiar to many readers.

Numerous other examples may be noted, e. g., ζ and δ Draconis; β and γ Andromedae; δ Herculis and β Cygni; ϵ Aquarii, γ and δ Sagittae; ι and ϵ Aquilae; β and δ Ophiuchi, γ and λ Aquarii; γ and κ Serpentis; γ and δ Persei; γ and δ Tauri, etc.

Only one star of class N was examined. This was 19 Piscium, having a magnitude of 5.3. It was compared with ϕ Pegasi which has the same magnitude, and belongs to class M. The class N star gave almost twice the deflection of the class M star. In fact 19 Piscium would have given a still larger deflection if correction had been made for air mass, for it had the greater zenith distance. This pair of stars represents the smallest magnitude upon which rigidly quantitative observations were made. Only one star of class N was conveniently at hand for observation, but from the measurements on numerous stars of class M as compared with the blue stars, it is to be expected that stars of class N will be found to have, as a general rule, the highest emission of all.

Some of the red stars have an abnormally low emission, as, for instance, α Arietis. Several stars, e. g., β Pegasi and α Herculis are conspicuous for the total amount of radiation emitted in proportion to their photometric brightness. They are binaries and the companion stars no doubt have some effect. Instead of causing a

deflection of several millimeters, they produced a deflection of 2 to 3 cm.

Of the double stars measured radiometrically, α Andromedae is an excellent example. The star A (magnitude = 2.28) belongs to class K, and the component, B C (magnitude = 5.1) is "blue." The intensity of the radiation from the latter is perhaps only about one-half that observed from a red star H. R. 7676 Draconis (class Ma), which has a magnitude of 5.4.

Time did not permit making a prolonged series of measurements on variable stars. The star α Herculis is an irregular variable. The radiation measurements recorded in Table 2, "II. Thermo-element No. 7 (1a)," undergo a large variation, but it can not be maintained that this is due entirely to a variation in the emission. In this connection it is interesting to note that frequently on repeating the observations on stars, the measurements were found in close agreement, as, for example, α Coronae Borealis and β Ophiuchi on August 4 and 9.

Sometimes the radiations from stars belonging to the same group are found to be in proportion to their photometric brightness. For example, α Aquilæ and α Ophiuchi, which belong to class A5. The ratio of their visual brightness is 3.02; and the ratio of their radiations is 2.96, which is a difference of only 2 per cent. The ratio of the intensities of the radiations from Arcturus and Vega is 2.4, which is in agreement with the observations of Nichols which gave a value of 2.2.

Among the red stars the relation between photometric brightness and total radiation is less exact than for blue stars. A good example is a comparison of several stars of class Ma. The star ϕ Pegasi (magnitude = 5.23) gave a deflection of 0.22 cm. The star λ Aquarii (magnitude = 3.84) gave a deflection of 1.02 cm, which is equivalent to 0.28 cm for a star having a magnitude of 5.23. Similarly, the reduced deflection (1.37 cm; magnitude = 3.03) of δ Ophiuchi would be 0.18 cm; of ν Ceti (deflection = 0.31; magnitude = 4.18) it would be 0.13 cm; and of α Orionis (deflection = 19.14 cm; magnitude = 0.92) it would be 0.34 cm. In all cases the deviations from the value observed for a 5.23 magnitude star are larger than the errors of observation. This direct relation

is of course not true, in general, and there is no reason why one should expect such a similarity. It is hardly to be expected that there are two stars having the same constitution and being in the same physical condition, although among the countless number in existence one may chance upon two having closely the same energy distribution.

In the measurements of the radiation from the rings of Saturn it is to be noticed that the receiver was a little larger than the image of the rings. Hence, the deflection is somewhat smaller (as compared with the observation on the central ball) than it would have been if the whole receiver had been exposed. No comparison can therefore be made with the deflection observed when the thermocouple was exposed to the central disk of Saturn.

In view of the fact that heretofore observers were glad to obtain any indication of the radiation from stars and planets, it is of interest to record that in observing the radiation from Venus it was necessary to place a resistance of 50 ohms in series with the galvanometer in order to reduce the sensitivity and thus keep the galvanometer deflection (which amounted to 127 cm) upon the scale.

V. MEASUREMENTS OF STELLAR RADIATION TRANSMITTED BY A CELL OF WATER

While the measurements of the total radiation from stars are interesting and instructive, they contain as unknown factors the size and distance of the stars and the amount absorbed by the earth's atmosphere. The really convincing data will be those pertaining to the spectral-energy curves of the stars. An approximate estimate of the energy in different parts of the spectrum may be obtained by using absorption cells. New difficulties are then introduced, the principal one being the change in focal length. In the present work the absorbing material was water, which is opaque to all the radiations of wave lengths longer than 1.4μ . The absorption cell consisted of a piece of plate glass 1 cm in thickness pierced by a hole 2 cm in diameter. The windows were of quartz, 2 mm in thickness. The faces of the windows were plane and very closely parallel. The focal length of the telescope was

lengthened 3 mm by insertion of the water cell, and this change in focal length was made when inserting the cell.

The telescope being in an inclined position, the hinged box, A, Fig. 4, containing the absorption cell, was opened by gravity, and it was raised in front of the thermocouples by pulling a fine wire, W, Fig. 4. The transmission was determined by exposing the thermoelement to a star and observing the galvanometer deflection with, and without the absorption cell in the path of the rays. If the total radiation from a red star contains more infra-red than does the total radiation from a blue star, then the amount transmitted by the water cell will be less for the red than for the blue star. This is the true condition of affairs, as may be noticed in Table 3, in which are given the transmissions for various stars. With but a single exception there is an exact similarity between the values of the transmissions and between the stellar classification. The blue stars (classes B, A) have the least infra-red radiations, as evidenced by the fact that from 60 to 70 per cent of the total radiation passed through the water cell. The only exception is β Orionis, which at this season of the year had to be observed at dawn, and errors may have been caused by the large amount of daylight.

TABLE 3

Transmission of Stellar Radiation Through a 1 cm Layer of Water

Object	Stellar class	Transmission in per cent	Remarks	Object	Stellar class	Transmission in per cent	Remarks
α Lyrae.....	A	58	(Vega).	Jupiter.....		65	Receiver in center of disk including part of dark band.
α Aquilae.....	A 5	69	(Altair).				
β Orionis.....	B 8 p	42	(Rigel). A low value for a blue star.			66	Receiver covers upper dark band.
α Auriga.....	G	48	(Capella).	Venus.....		59	
α Boötis.....	K	45	(Arcturus).	Saturn.....		55	Receiver covers central disk.
α Tauri.....	K 5	35	(Aldebaran).				
γ Draconis...	K 5	32		Moon.....		14.7	
β Pegasi.....	M b	29					
α Orionis.....	M a	27	(Betelgeux).				
α Scorpii.....	M a p	27	(Antares).				
α Herculis...	M b	21					

The yellow stars are easily arranged according to their transmissions. For example, the transmission of a class G star (Capella) is 48 per cent and a class K5 star is 32 per cent.

The red stars (class M) emit the most infra-red, only about 25 per cent of their radiations passing through the water cell. From this it appears that about 60 per cent of all the radiation coming from a blue star lies in the spectral region to which the eye is sensitive, while only 20 to 30 per cent of the total radiation from a red star affects the eye. This brings out very clearly why it is that a red star of the same photometric brightness as a blue star emits from two to three times as much total radiation, as was observed. For a rough comparison it may be stated that blue stars emit two times as much "light" as the yellow stars and three times as much as the red ones.

The absorption cell tells us nothing of the size and the distance of the stars. It simply indicates that the spectral energy distribution is such that for a blue star from 50 to 60 per cent of the total energy lies in the visible and in the ultra-violet part of the spectrum. This may be the result of a difference in the emissivity of the photosphere, which is considered to be composed of incandescent helium and hydrogen. The photosphere of red stars is considered to be cooler, and to be composed of metallic vapors. From our knowledge of the energy distribution in the spectra of gases in vacuum tubes, it appears that usually, for incandescent gases, there is but little infra-red radiation. However, in incandescent helium²⁸ there is a great amount of infra-red radiation. Whether this is the cause of the low transmission for the radiations from β Orionis, whose spectrum shows incandescent helium, is of course an unanswered question. It is to be noted that β Orionis (class B8p) is a spectroscopic binary, and it is highly probable that the low transmission through the water cell is due to the large amount of infra-red emitted by a red component which contributes but little to the visual brightness of this star.

The transmissions observed for the solar rays reflected from the planets are very closely the same as the albedos. The albedo of Jupiter is about two-thirds (i. e., 0.66), while the albedo of the Moon is about one-sixth (i. e., 0.16). In the case of Jupiter the

²⁸ This Bulletin, 9, p. 81; 1912.

solar rays do not penetrate the atmosphere, which is warmed but little. The transmission of the reflected rays is therefore closely that of the direct solar rays. In the case of the Moon the transmission is only about 15 per cent. This is evidently due to a warming of the lunar surface, as a result of exposure to the solar rays, and this in turn radiates heat waves which are not transmitted by the absorption cell. The question whether these infra-red rays of long wave lengths are a result of reradiation or whether they are partly solar rays which are selectively reflected from the lunar surface has been discussed elsewhere,²⁹ and the matter has been left in doubt. In these measurements on the Moon the receiver was set near the edge, about 15° north latitude and 80° west longitude, near the Mare Crisium, the age of Moon being about seven days.

Measurements were made on the composition of the light in the bright and the dark bands of Jupiter. Both gave the same transmission through the water cell, showing that whatever may be the cause of the dark bands the diminution in brightness is quite non-selective as regards the infra-red. The observations should, of course, be repeated, and continued over a long period, so as to include other portions of the surface of the planet. Further work should be done on stars, using different absorption cells which isolate narrow regions of the spectrum. This is, of course, a poor substitute for the direct measurement of spectral-energy curves of stars, so frequently mentioned in this paper.

VI. ATMOSPHERIC TRANSPARENCY FOR STELLAR RADIATIONS

Atmospheric conditions on Mount Hamilton are unusually uniform during the summer months. On August 8, 9, and 12 conditions were sufficiently uniform so that when the galvanometer deflections were reduced to the same sensitivity, $i = 1 \times 10^{-10}$ ampere, the deflections observed on γ Draconis, which was used as a reference standard, were in agreement within 3 per cent. (See Table 2, "II. Thermoelement No. 7 (1a).") Conditions suddenly changed on August 13, so that the deflections for Vega were only half as large as was usually observed.

²⁹ Publication No. 65, p. 110, Carnegie Institution of Washington; 1956.

The great difference in atmospheric transparency for different classes of stars is illustrated by the measurements on the following stars which were observed at closely the same hour on two consecutive nights. The ratio of the galvanometer deflections for August 17: August 16 was 1.18 for α Lyrae (class A; a blue star) and 1.49 for α Herculis (class Ma; a red star). In other words, on August 16 the atmosphere absorbed 18 per cent more of the radiations from a blue star (α Lyrae) and 49 per cent more of the radiations from a red star (α Herculis) than on the following night. As recorded elsewhere, the humidity on August 17 was unusually low as compared with most of the other nights during which observations were made.

From the foregoing it is evident that the values of the radiation from different stars, as given in the last column of Table 2, can not be exact when comparison is made of measurements obtained on different nights. This is owing to the fact that the factors used are usually those obtained by measurements on a blue star, when measurements should also have been made on red stars. The factors used for reducing all the observations to a uniform value are given in Table 4. For convenience, the data of July 30 are used as a basis of reference.

TABLE 4

Factors for Reducing the Galvanometer Deflections to the Same Sensitivity as Used on July 30, 1914

Date of observations	Reduction factor	Thermoelement used	Date of observations	Reduction factor	Thermoelement used
		Number			Number
July 30.....	1.00	6 (3 b)	Aug. 15.....	1.45	7 (1 a)
Aug. 1.....	2.00	6 (3 b)	Aug. 16.....	1.28	7 (1 a)
Aug. 3.....	1.06	6 (3 b)	Aug. 17.....	1.00	7 (1 a)
Aug. 4.....	1.17	7 (1 a)	Aug. 19.....	1.00	7 (1 a)
Aug. 8.....	1.27	7 (1 a)	Aug. 20.....	1.38	7 (1 a)
Aug. 9.....	1.27	7 (1 a)	Aug. 24.....	.80	6 (3 b)
Aug. 12.....	1.27	7 (1 a)	Aug. 25.....	.85	6 (3 b)
Aug. 13.....	1.40	7 (1 a)			

In Table 4 the factor for reducing the galvanometer deflections to July 30 are less than unity for the data obtained on August 24 and August 26. This is due in part to the fact that the dust had been removed from the mirror and the surface polished.

1. REDUCTION OF THE OBSERVATIONS TO THE ZENITH

The radiometric observations on the stars and planets having been made at widely different zenith distances, some correction for the differences in atmospheric absorption should perhaps be applied. This correction will be different for different classes of stars, and to a minor degree different for every star. Such corrections are not available, and if applied they would add but little to the usefulness of the data.

In comparing the total radiation from stars having the same photometric brightness, but differing in color, pairs of stars were selected which had closely (1) the same declination, and (2), when convenient, also closely the same right ascension. The first eliminated to some extent the air mass, and the second eliminated a possible change in the radiation sensitivity of the vacuum thermocouple. Aside from these comparisons of pairs of stars, the measurements on individual stars were made in order to obtain some idea of the sensitivity that will be required in order to obtain their spectral energy curves.

VII. THE ABSOLUTE VALUE OF THE TOTAL RADIATION FROM THE STARS

It is of interest to obtain a rough estimate of the total amount of heat received from stars, as compared with the heat received from the sun (transmitted through the atmosphere), which is of the order of 1 g-cal per cm² per minute. This is accomplished by exposing the receivers to a standard of radiation,²⁰ using a standard galvanometer sensitivity of $i = 1 \times 10^{-10}$ ampere. Under these conditions for thermoelement No.6 (3b) a deflection of 1 mm = 1.22×10^{-10} watt = 17.4×10^{-10} g-cal per minute (area = 0.089 mm²). The ratio of apertures being 1:7 000 000 when using the large reflecting telescope, a deflection of 1 mm = 25×10^{-17} g-cal per minute. This is the intensity of the radiation which is falling upon an area of the mirror equal in size to that of the receiver, viz, 0.089 mm². Hence, when the observed deflection is 1 mm, the energy falling upon 1 cm² of the mirror is $25 \times 10^{-17} \times \frac{100}{0.089} = 28 \times 10^{-14}$ g-cal per cm² per minute. This is the value obtained as

²⁰ This Bulletin, 11, p. 87; 1914.

a result of a test of the sensitivity of the instrument after returning from Mount Hamilton. It agrees well with the candle test made at the observatory. Assuming that the radiation from this candle²¹ was 17.5×10^{-8} g-cal per mm² per minute, then the total radiation falling upon the receiver was $17.5 \times 10^{-8} \times 0.089 = 1.55 \times 10^{-8}$ g-cal per minute. The observed deflection being about 1000 mm, 1 mm = 15.5×10^{-10} g-cal per minute; or, when using the large reflector, having an aperture ratio of 1:7 000 000, a deflection of 1 mm = 22×10^{-17} g-cal per minute.

This, as in the preceding computation, is the intensity of the radiation which is falling upon an area of the mirror equal in size to that of the receiver. Hence, the energy falling upon 1 cm² of the mirror is $22 \times 10^{-17} \times \frac{100}{0.089} = 25 \times 10^{-14}$ g-cal per cm² per minute. The radiation sensitivity (in absolute measure) of the thermoelement No. 7 (1a) was determined before going to and after returning from Mount Hamilton. In the meantime the quartz tube containing calcium had been replaced. The radiation sensitivity tests, made before and after the work was completed, were in agreement within 4 per cent, which is closer than should be expected. For this receiver (area = 0.113 mm²) a deflection of 1 mm = 1.54×10^{-10} watt = 22×10^{-10} g-cal per minute.

The ratio of apertures of the receivers being 1:5 700 000 when the thermoelement was in the focus of the large reflector, a deflection of 1 mm = 38×10^{-17} g-cal per minute. This represents the intensity of the radiation on 0.113 mm² of the mirror. Hence, a deflection of 1 mm = $38 \times 10^{-17} \times \frac{100}{0.113} = 34 \times 10^{-14}$ g-cal per cm² per minute. This value is larger than the one obtained for No. 6 (3b), as it should be; for the sensitivity is about 25 per cent smaller, as observed in the tests on stars.

The difference in sensitivity (for No. 6 (3b), 1 mm = 25 to 28×10^{-14} g-cal; No. 7 (1a), 1 mm = 34×10^{-14} g-cal) amounts to about 20 per cent. This, as just stated, is in agreement with the tests on stars using the Crossley reflector. For it is to be noted that errors arise due to the difficulty in estimating the total area of the receiver exposed when making the tests on the standard lamp.

²¹ This Bulletin, 11, p. 87; 1914.

The receiver No. 7 (1a) having been used in making most of the observations, the data pertaining to the sensitivity of this receiver were therefore used in making the following computations. Using the value 1 mm deflection = 34×10^{-14} g-cal per cm^2 per minute, for a star giving a deflection of 1 mm, it would take

$$\left(\frac{1}{34 \times 10^{-14}} = \right) 3 \times 10^{13} \text{ minutes or } 6 \times 10^6 \text{ (i. e., six million) years}$$

to raise the temperature of 1 gram of water 1°C . The star Polaris is an excellent example. It produced a galvanometer deflection of 6 mm. Hence, the amount of radiation from Polaris incident upon 1 cm^2 of the earth's surface is $(6 \times 34 \times 10^{-14} =) 2 \times 10^{-13}$ g-cal per cm^2 per minute. At this rate it would require the radiations from Polaris to fall upon 1 cm^2 continuously for one million years in order to raise the temperature of 1 g of water 1°C ; assuming that, in the meantime, all the incoming radiations are absorbed, and that no heat is lost by conduction, convection, or radiation. In contrast with this value the radiation from the sun which falls upon an area of 1 cm^2 , is sufficient to raise the temperature of 1 g of water 1°C in about one minute.

Various estimates have been made of the light of all the stars. Chapman²² calculates that the total light of all the stars is equivalent to that from about 1000 stars of the first magnitude, or that of about 2500 stars as bright as Polaris, which is a second magnitude star. Newcomb's value is about 5000, and Kapteyn's value is about 6000 stars of the second magnitude.

As for the distribution of the bright stars, according to Campbell's²³ examination of 6100 stars brighter than the six and twenty-five one hundredths visual magnitude, they are distributed (in round numbers) as follows: Blue stars (A, B) = 2600, yellow stars (F, G, K) = 3000, and red stars (M) = 500. Of this number there are about as many stars in class K as in class A and about one-third as many in class M. Taking as an extreme case a red star of the second magnitude instead of Polaris, the observations to be found in the tabulated data given in this paper show that the galvanometer deflections for red stars were four to five times those obtained on Polaris, viz, deflections of 25 to 30 mm. Hence, for 2500 to 5000

²² Chapman, *Monthly Notices, Roy. Astronom. Soc.*, 74, p. 446, 1914.

²³ Campbell, *Stellar motions*, p. 154.

stars as bright as Polaris, the total radiation (the equivalent galvanometer deflection) would be 70 000 to 150 000 mm. Of this amount only perhaps one-third would be effective upon a radiometric instrument exposed to the sky; the total radiation incident upon a horizontal surface being 1 to 2×10^{-8} g-cal per cm^2 per minute. At this rate it would require the total stellar radiations incident upon 1 cm^2 of the earth's surface to be absorbed and conserved continuously for a period of 100 to 200 years in order to raise the temperature of 1 g of water 1°C . Evidently the incoming stellar radiation can contribute but little in retarding the cooling of the earth. For the measurements of nocturnal radiation, which is usually a loss of terrestrial radiation into space, indicate that for a lampblack surface the outgoing radiation may be as high as 0.1 the solar constant. The emissivity of the materials forming the earth's surface may be much lower than this, say 0.01 g-cal per cm^2 per minute. The practical application of this data is that, in measurements of nocturnal radiation, the correction for the incoming stellar radiation is entirely negligible.

VIII. SUMMARY

In the foregoing pages experiments are described showing that there is but little difference in the radiation sensitivity of stellar thermocouples constructed of bismuth—platinum and thermocouples of bismuth—bismuth tin alloy, which have a 50 per cent higher thermoelectric power.

Improvements are described in the method of maintaining a vacuum by means of metallic calcium, whereby it will be possible to go to the remotest station for making radiation measurements without carrying an expensive vacuum pump.

With this outfit measurements were made on the radiation from 112 celestial objects, including 105 stars. This includes measurements on the bright and the dark bands of Jupiter (also a pair of his satellites), the rings of Saturn, and a planetary nebula. Quantitative measurements were made on stars down to the five and three-tenths magnitude; and qualitative measurements were made on stars down to the six and seven-tenths magnitude.

It was found that red stars emit from two to three times as much *total* radiation as blue stars of the same photometric magnitude.

Measurements were made on the transmission of the radiations from stars and planets through an absorption cell of water. By this means it was shown that of the total radiation emitted, the blue stars have about two times as much *visible* radiation as the yellow stars, and about three times as much *visible* radiation as the red stars.

A stellar thermocouple and a bolometer were compared and the former was found to be the more sensitive. The conclusion arrived at is that from the appearance of the data at hand greater improvements are to be expected in stellar thermocouples than in stellar bolometers.

The object of the investigation was to obtain some estimate of the sensitivity required in order to be able to observe spectral energy curves of stars. The radiation sensitivity of the present apparatus was such that, when combined with a 3-foot reflecting telescope, a deflection of 1 mm would have resulted when exposed to a candle placed at a distance of 53 miles. In order, however, to do much successful work on stellar spectral energy curves, a sensitivity 100 times this value is desirable. In other words, assuming that the rays are not absorbed in passing through the intervening space, the radiometric equipment (radiometer and mirror) must be sufficiently sensitive to detect the radiation from a candle removed to a distance of 500 miles. This can be accomplished by using a 7-foot mirror and by increasing the sensitivity of the present radiometer (thermocouple and galvanometer) 20 times. This increase in sensitivity is possible.

Measurements were made to determine the amount of stellar radiation falling upon 1 cm² of the earth's surface. It was found that the quantity is so small that it would require the radiations from Polaris falling upon 1 cm² to be absorbed and conserved continuously for a period of one million years in order to raise the temperature of 1 g of water 1° C. If the total radiation from all the stars falling upon 1 cm² were thus collected and conserved, it would require from 100 to 200 years to raise the temperature of

1 g of water 1° C. In marked contrast with this value, the solar rays, which reach the earth's surface, can produce the same effect in about 1 minute.

IX. ACKNOWLEDGMENTS

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